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REGISTERED NO. M 3121

PROCEEDINGS

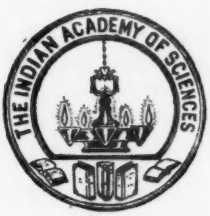
OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XXVI] *SECTION A* [NO. 4

OCTOBER, 1947



Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO,
SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES,
BANGALORE.

GENERALISED ALGEBRA OF ELEMENTARY PARTICLES*

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Received September 8, 1947

1. Introduction

Generalising the well-known result that the wave equations of the electron and the meson can both be put in the linear form

$$\partial_\mu \beta_\mu \psi + \chi\psi = 0 \qquad (\mu = 1, 2, 3, 4) \tag{1}$$

it has been shown elsewhere[6,7,8] that, under suitable assumptions, (1) can also be taken as the wave equation for a particle of arbitrary spin. This is shown possible by postulating the relativistic invariance of (1), and that the spin operator $t_{\mu\nu} = is_{\mu\nu}$ satisfies in every case the equation

$$t_{\mu\nu} = (\beta_\mu \beta_\nu - \beta_\nu \beta_\mu) \equiv (\beta_\mu, \beta_\nu). \tag{2}$$

These assumptions with the further one that the eigen-values of the spin operator for a particle of spin r are $r, r-1, \ldots -r+1, -r$ enable the setting up of a hypercomplex algebra generated by the symbols β_μ and the unit element, reducing in the particular cases of $r = \frac{1}{2}$, and $r = 1$ to the Dirac and meson algebras respectively. The algebra for the case $r = \frac{3}{2}$ can also be dealt with in a simple manner as shown in detail elsewhere.[8]

The particular case of the algebra of meson matrices has been generalised by Schrödinger[9] and Kemmer[3]‡ for the case where more than four elements β_μ exist. The former has considered the case of five elements, and the latter the case of an arbitrary number s of elements. The object of the present paper is to show that this generalisation from four to s elements β_μ is also possible in the case of the algebra associated with a particle of arbitrary spin r or $r + \frac{1}{2}$.

The method adopted in showing this is based on the result deduced by Bhabha[1,2] as a consequence of (2) that the problem of finding irreducible

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* Paper read before the Annual Conference of the Indian Academy of Sciences at Allahabad, December 1946.

‡ This reference will be denoted hereafter as K.

representations of the β-algebra is the same as that of finding all irreducible representations of the Lorentz group in five dimensions (see also Lubański[5]). In fact, this result follows from the relations

$$(\beta_\mu, t_{\mu\nu}) = \beta_\nu; \ (t_{\mu\nu}, \beta_\nu) = \beta_\mu \tag{3}$$

which are immediate consequences of (2), and the relativistic invariance of (1). Further, as is well known, the above problem concerning the Lorentz group in five dimensions is identical with the corresponding problem for the real orthogonal group in five dimensions except for the formal process of assigning imaginary values to the parameters involved. It is obvious that, if the relations (2) and (3) also hold when there are s elements β_μ, the representations of the corresponding β-algebra would be the same as those of the real orthogonal group of $s+1$ dimensions.

Employing this method, we use the well-known results relating to the real orthogonal group of n dimensions ($n = 2k+1$ or $2k$) to derive the number and order of the several irreducible representations of the generalised s-element β-algebra corresponding to spin r and $r+\frac{1}{2}$ (r being a positive integer). In particular, for $r=1$ we get an alternative derivation of Kemmer's results for the meson algebra, and equally simple results for the algebra of spin $\frac{3}{2}$.

2. Method of Deriving Representations

An alternative formulation of the theory of the linear wave equation (1) has been given by Kramers, Belinfante and Lubański[4] in terms of quantities known as *undors* which transform like products of several Dirac spinors. On this formulation, the wave function in (1), for the general case of spin r, would be an undor of rank $2r$ (= N) and has 4^N components. The matrices β_μ are given by

$$\beta_\mu = \sum_{j=1}^{N} \gamma_{(j)}{}^{\mu}$$

and,

$$\underset{(j)}{\gamma^\mu} = \underset{(1)}{I} X \ldots . X \underset{(j)}{\gamma^\mu} X \ldots . X \underset{(N)}{I}$$

I being the unit matrix, X the direct product, $\gamma_{(j)}{}^{\mu}$ Dirac matrices which commute for different values of j. This representation of the β_μ's is identical with the general spinor representation discovered by Cartan for the orthogonal group and investigated by Brauer and Weyl in detail (see Weyl[11]). As shown by them, every representation of the n-dimensional orthogonal group is contained in the Kronecker product of a certain basic representation with itself taken a sufficient number of times.

Accordingly we assume that the representations of the algebra generated by the β_μ's are contained in the direct product

$$\Delta \text{ X} \ldots . (2r \text{ or } 2r+1 \text{ times}) \ldots . \text{X } \Delta \tag{4}$$

according as the spin is r or $r+\frac{1}{2}$, where Δ is the basic spin representation of the rotation group in n dimensions (see Murnaghan*[10]). Any general representation of the orthogonal group specified by the k parameters

$$\lambda_1 \geqslant \lambda_2 \geqslant \ldots . \geqslant \lambda_k \geqslant 0 \qquad (n = 2k+1, \text{ or } 2k)$$

is denoted by $\Gamma_{(\lambda)}$, and the basic representation would, in this notation, be $\Gamma_{(1/2)^k}$. The successive direct products of Δ by itself can be analysed according to the rule [M., p. 313 (10·21)]

$$\Delta \text{ X } \Gamma_{(\lambda)} = \Sigma\, \Gamma_{(p+\frac{1}{2})} \tag{5}$$

the summation on the right being over the 2^k sets (p) which are obtained from the set (λ) by either replacing λ_j by $\lambda_j - 1$ or by leaving it unaltered (it being understood that any set (p) for which the normal non-increasing order is not preserved or which contains a negative number is to be dropped).

The order of any representation $\Gamma_{(\lambda)}$ is given by M. (10·22) and (10·27) or by the equivalent formulæ [M. (9·46) and (9·47), p. 260]

$$d_{(\lambda)} = \frac{2^k}{(2k-1)!\ldots.3!!!} l_1' \ldots . l_k' \left\{ \prod_{(p<q)}^{k} (l_p'^2 - l_q'^2) \right\} \tag{6, a}$$

for the case $n = 2k+1$, and

$$\left.\begin{aligned} d_{(\lambda)} &= \frac{2^k}{(2k-2)!\ldots.4!2!} \prod_{(p<q)}^{k} (l_p^2 - l_q^2);\ l_k \neq 0 \\ &= \frac{2^{k-1}}{(2k-2)!\ldots.4!2!} \prod_{(p<q)}^{k-1} (l_p^2 - l_q^2);\ l_k = 0 \end{aligned}\right\} \tag{6, b}$$

for the case $n = 2k$,

where $$l_1 = \lambda_1 + (k-1),\ l_2 = \lambda_2 + (k-2), \ldots . , l_k = \lambda_k \tag{7}$$

and $$l_p' = l_p + \tfrac{1}{2}$$

If we consider the algebra of the s elements β_μ, the order of the corresponding orthogonal group is $s+1$, so that we write

$$\left.\begin{aligned} & n = s+1 \\ \text{and for } s \text{ even}, \quad & n = 2k+1 \text{ or, } k = \tfrac{1}{2}s \\ \text{for } s \text{ odd}, \quad & n = 2k \text{ or, } k = \tfrac{1}{2}(s+1) \end{aligned}\right\} \tag{8}$$

* This reference will be denoted hereafter as M.

3. Meson Algebra and Algebra for Spin 3/2

Let us first consider the meson algebra. The representations of this algebra are contained in the direct product $\Delta \times \Delta$ whose analysis is explicitly given in M. (10·14), p. 309 as

$$\Delta \times \Delta = \begin{Bmatrix} \Gamma_0 + \ldots + \Gamma_k \\ + \Gamma_0^* + \ldots + \Gamma_k^* \end{Bmatrix}; \; n = 2k+1 \qquad (9, a)$$

$$\Delta \times \Delta = \begin{Bmatrix} \Gamma_0 + \ldots + \Gamma_{k-1} \\ + \Gamma_0^* + \ldots + \Gamma_{k-1}^* \end{Bmatrix} + \Gamma_k \, (= \Gamma_k' + \Gamma_k''); \; n = 2k \qquad (9, b)$$

Since Γ and Γ^* coincide over the rotation group, we have $(k+1)$ or $(k+2)$ representations according as $n = 2k+1$ or $2k$. The additional representation in the latter case is due to the fact that for $n = 2k$, the two-valued representation Γ_k is the sum of two irreducible inequivalent representations Γ_k' and Γ_k'' of equal orders. In fact, these are the *twin representations* of Kemmer for the case where the number of elements s is odd (K, p. 191). Thus it follows from (8) that the number of representations is $\frac{1}{2}s + 1$ or $\frac{1}{2}(s+5)$ according as s is even or odd [K., p. 192, (8)]. If we discard Γ_0 as belonging to the ablgera corresponding to the lower spin 0, the number of representations would be $\frac{1}{2}s$ or $\frac{1}{2}(s+3)$ according as s is even or odd.

To determine the order d_i of the representation Γ_i in (9, *a*) or (9, *b*), we write the set $(\lambda) = (\lambda_1, \ldots, \lambda_k)$ as $(\lambda_1 = \ldots = \lambda_i = 1; \; \lambda_{i+1} = \ldots = \lambda_k = 0)$, and use (6, *a*) or the second equation of (6, *b*) respectively (since $l_k = 0$). In evaluating the expressions $\Pi (l_p^2 - l_q^2)$ and $\Pi (l_p'^2 - l_q'^2)$ appearing in (6), it introduces simplification if we notice that in the sequence $(l_1, l_2, \ldots, l_k)$ or $(l_1', l_2', \ldots, l_k')$ there is a gap between l_i and l_{i+1}, supply this missing term, and compensate by dividing by the product of the additional squared differences. This procedure leads in the case (6, *a*) to

$$d_i = \frac{2^k}{(2k-1)! \ldots 3!\, 1!} \cdot \frac{(2k+1)(2k-1)\ldots 1}{2^k (2k-2i+1)} \cdot (2k)!\,(2k-2)! \ldots 2!$$
$$\div \{i!\,(2k-2i+2)\ldots(2k-i+1)\}\,\{(k-i)!\,(k-i+1)\ldots(2k-2i)\}$$
$$= \frac{(2k-1)!}{i!\,(2k-i+1)!}$$

$$i.e., \quad d_i^{(s)} = \binom{2k+1}{i} = \binom{s+1}{i} \qquad (10)$$

The same result is obtained in the case $n = 2k$ when we use the second equation of (6, *b*). Putting $i = k$, gives, in this case, the order of

Γ_k as $\binom{2k}{k}$, so that each of the twin representations has the order

$$\tfrac{1}{2}\binom{2k}{k} = \tfrac{1}{2}\binom{n}{\frac{1}{2}n} = \tfrac{1}{2}\binom{s+1}{\frac{1}{2}s+\frac{1}{2}}$$

The relation

$$\binom{2k+1}{i} = \binom{2k}{i} + \binom{2k}{i-1}$$

shows that two representations of $(s-1)$ generate one of s. Also, the relation

$$\binom{2k-1}{k-1} = \tfrac{1}{2}\binom{2k}{k}$$

shows that the order of each of the twin representations for odd s is equal to that of the highest representation of $(s-1)$. These results are in accord with those contained in Kemmer's paper (see K, p. 194).

We shall next consider the generalised algebra of spin 3/2 with s symbols β_μ. The representations are given by $\Delta \mathrm{X} \Delta \mathrm{X} \Delta$, and using (9) and writing $\Delta \mathrm{X} \Delta = \sum_0^k \Gamma_i$, we have (for $n = 2k+1$)

$$\Delta\mathrm{X}\,\Delta\mathrm{X}\,\Delta = \sum_{i=0}^{k} \Delta \mathrm{X}\, \Gamma_i = \sum_{i=0}^{k} \Delta \mathrm{X}\, \Gamma_{(1)^i (0)^{k-i}}$$

Analysis by rule (5) leads to

$$\Delta\mathrm{X}\,\Delta\mathrm{X}\,\Delta = \sum_{i=0}^{k} (k-i+1)\, \Gamma_{(\frac{3}{2})^i (\frac{1}{2})^{k-i}} \qquad (11)$$

Thus for even s, there are $(k+1)$ representations given by $\Gamma_{(\frac{3}{2})^i (\frac{1}{2})^{k-i}}$ $(i = 0, \ldots, k)$, *i.e.*, $\frac{1}{2}s + 1$ just as in the meson algebra. For the case of odd s the number of representations is again $k+2 = \frac{1}{2}(s+5)$ as in the meson case since the representation $\Gamma_{(\frac{3}{2})^k}$ is the sum of two twin representations $\Gamma'_{(\frac{3}{2})^k}$ and $\Gamma''_{(\frac{3}{2})^k}$. Discarding in this case $\Gamma_{(\frac{1}{2})^k}$ as belonging to the lower spin $\frac{1}{2}$, *i.e.*, to the s-element Dirac algebra, the number would be $\frac{1}{2}s$ or $\frac{1}{2}(s+3)$.

To determine the order of the representation $\Gamma_{(\frac{3}{2})^i (\frac{1}{2})^{k-i}}$, we write $\lambda_1 = \lambda_2 = \ldots = \lambda_i = 3/2$; $\lambda_{i+1} = \ldots = \lambda_k = \frac{1}{2}$, and use (6).

(i) s even, n odd $= 2k+1$; (6, *a*) gives

$$d_i = \frac{2^k (2k+1)!}{i!\,(2k-i+1)!}\binom{2k-2i+2}{2k-i+2}$$

i.e.,
$$d_i = 2^k \left\{\binom{2k+1}{i} - \binom{2k+1}{i-1}\right\} = 2^{\frac{1}{2}s} \left\{\binom{s+1}{i} - \binom{s+1}{i-1}\right\} \qquad (12, a)$$

(ii) s odd, n even $= 2k$; the first equation of (6, b) gives (since $l_k \neq 0$)

$$d_i = \frac{2^k (2k)!}{i!\,(2k-i)!}\left(\frac{2k-2i+1}{2k-i+1}\right)$$

$$= 2^k \left\{\binom{2k}{i} - \binom{2k}{i-1}\right\} = 2^{\frac{1}{2}(s+1)} \left\{\binom{s+1}{i} - \binom{s+1}{i-1}\right\} \qquad (12, b)$$

Equations (12, a) and (12, b) are simple generalisations of (10) to the case of spin $\frac{s}{2}$.

That the order of the twin representations for odd s is equal to that of the highest representation for $(s-1)$ also follows immediately from the identity

$$2^{k-1}\left\{\binom{2k-1}{k-1} - \binom{2k-1}{k-2}\right\} = \tfrac{1}{2}\cdot 2^k \left\{\binom{2k}{k} - \binom{2k}{k-1}\right\}$$

which can be easily verified.

For the special case of $s = 4$, *i.e.*, the usual case of four β_μ's the equation (12, a) gives the orders of the three representations (corresponding to $i = (0, 1, 2)$ as 4, 16, 20 (see reference 8), and (11) gives the analysis of the triple product of Δ into these components. Since in this case the wave function in (1) is an undor of rank 3 with $4^3 = 64$ components, equation (11) can be expressed by saying that the undor representation for spin $\frac{3}{2}$ contains the 20th order representation once, the 16th order twice, and the Dirac representation thrice, giving the check by degrees,

$$64 = 20 + (2 \times 16) + (3 \times 4).$$

For the general case of s elements also we can obtain the correct check by degrees using (11). Writing $\Delta = \Gamma_{(\frac{1}{2})^k}$, (6) gives the order of this basic representation as 2^k (both for n odd or even). (11) shows that $\Gamma_{(\frac{s}{2})^i\,(\frac{1}{2})^{k-i}}$ is contained $(k-i+1)$ times in $\Delta \mathrm{X}\, \Delta \mathrm{X} \Delta$, and considering $n = 2k+1$, (12, a) gives the sum of the orders of the $(k+1)$ representations (including the Dirac representations) as

$$\sum_{i=0}^{k} (k-i+1)\cdot 2^k \left\{\binom{2k+1}{i} - \binom{2k+1}{i-1}\right\}$$

$$= 2^k (n\,\mathrm{C}_0 + n\,\mathrm{C}_1 + \ldots . + n\,\mathrm{C}_k)$$

$$= \tfrac{1}{2}\cdot 2^k (n\,\mathrm{C}_0 + n\,\mathrm{C}_1 + \ldots . + n\,\mathrm{C}_n) \text{ since } n \text{ is odd,}$$

$$= \tfrac{1}{2}\cdot 2^k \cdot 2^{2k+1} = 2^{3k}$$

which is equal to the order of the direct product $\Delta \mathrm{X}\, \Delta \mathrm{X}\, \Delta$ since Δ is of order 2^k.

For the case $n = 2k$, a correct check by degrees using (12, b) requires that the representations Γ_i $(i = 0, \ldots, \overline{k-1})$ should each appear twice as

many times as they do in the case $n = 2k + 1$. The same situation also holds in the meson case as can be seen from the table given by Kemmer (K, p. 195).

4. Algebra for Spins r and $r + \frac{1}{2}$

The derivation of the representations for $r = \frac{3}{2}$ from those of $r = 1$ suggests that a typical representation in the general case of r and $r + \frac{1}{2}$ would be of the forms

$$\Gamma_{(r)^{k-i_1}\,(r-1)^{i_1-i_2}\ldots(1)^{i_{r-1}-i_r}\,(0)^{i_r}} \qquad \text{(spin } r\text{)} \qquad (13,\ a)$$

and,

$$\Gamma_{(r+\frac{1}{2})^{k-i_1}\,(r-\frac{1}{2})^{i_1-i_2}\ldots(\frac{3}{2})^{i_{r-1}-i_r}\,(\frac{1}{2})^{i_r}} \qquad \text{(spin } r+\tfrac{1}{2}\text{)} \qquad (13,\ b)$$

labelled by r indices $i_1, i_2, \ldots i_r$ $(i_1 \geqslant i_2 \geqslant \ldots \geqslant i_r \geqslant 0)$ taking the values

$$\left.\begin{aligned} &i_r = 0, 1, 2, \ldots i_{r-1} \\ &\ldots\ldots\ldots\ldots\ldots \\ &i_j = 0, \ldots\ldots\ldots i_{j-1} \\ &i_2 = 0, \ldots\ldots\ldots i_1 \\ &i_1 = 0, \ldots\ldots (k-1) \end{aligned}\right\} \qquad (14)$$

The restriction of the values of i_1 in (14) from 0 to $(k - 1)$ instead of 0 to k serves to eliminate those representations which belong to the lower spins $(r - 1)$ and $(r - \frac{1}{2})$ as can be seen from (13, *a*) and (13, *b*) respectively. It is also to be noticed that the order in which the representations are numbered by the suffixes $i_1, i_2, \ldots i_r$ in (13) is different from the order adopted in the particular case of $r = 1$. In fact, putting $i_2 = i_3 = \ldots = i_r = 0$, the representation denoted by the single index i_1 would correspond to Γ_{k-i_1} in the notation of the previous article. We shall however denote the representation given by (13) as $\Gamma_{i_1, i_2 \ldots i_r}$ and derive the total number of these for the spins r and $r + \frac{1}{2}$. It is obvious that the number is the same for both the spins.

This total number is the same as the number of ways of choosing the indices subject to the conditions (14). For a given i_j the index i_{j+1} takes on $(i_j + 1)$ values, *viz.*, $(0, 1, \ldots, i_j)$ while i_1 takes on k values, *viz.*, $(0, 1, \ldots k-1)$. Thus the number required is the number of ways of choosing r things out of $(r + k - 1)$, and hence

$$\text{number of representations} = \binom{k+r-1}{r} \qquad (15)$$

We shall add a proof by induction. Assuming the truth of (15) for r we obtain the number of representations for $(r + 1)$ with the aid of the typical

one (r integral)

$$\Gamma_{(r+1)^{k-i_1}(r)^{i_1-i_2}\ldots(0)^{i_{r+1}}} \qquad (13, c)$$

as $\sum_{i_1=0}^{(k-1)} \binom{i_1+r}{r}$, since in (13, c) the index i_2 assumes values from 0 to i_1. But

$$\sum_{i_1=0}^{k-1} \binom{i_1+r}{r} = \sum_{l=1}^{k} \binom{l+r-1}{r}$$

$$= \sum_{l=1}^{k} \left\{ \binom{l+r}{r+1} - \binom{l+r-1}{r+1} \right\} \text{ using } n\mathrm{C}_{r-1} = (n+1)\,\mathrm{C}_r - n\mathrm{C}_r$$

$$= \binom{k+r}{r+1} - \binom{r}{r+1}$$

$$= \binom{k+r}{r+1}, \text{ since the second term vanishes}$$

which is (15) wth $(r+1)$ in place of r. Also (15) is true for $r=1$, and hence the validity of (15) is proved for general r.

The representation of the highest order is given by putting $i_1 = i_2 = \ldots = i_r = 0$ as $\Gamma_{(r)^k}$ or $\Gamma_{(r+\frac{1}{2})^k}$, and in the case $n = 2k$, this is a two-valued representation which is the sum of two irreducible inequivalent '*twin*' representations of equal orders. Thus we have (both for spins r and $r+\frac{1}{2}$)

(i) for s even, $n = s+1 = 2k+1$,

$$\text{no. of representations} = \binom{k+r-1}{r} = \binom{s+r-1}{r} \qquad (15, a)$$

(ii) for s odd, $n = s+1 = 2k$,

$$\text{no. of representations} = \binom{k+r-1}{r} + 1 = \binom{\frac{1}{2}s+r-\frac{1}{2}}{r} + 1 \qquad (15, b)$$

In the usual case of $s=4$, *i.e.*, $k=2$, (15, a) gives the number as $\binom{r+1}{r} = (r+1)$. For $r=1$, we get the results already obtained for the meson case.

Next to determine the order of the typical representation $\Gamma_{i_1, i_2, \ldots i_r}$, we consider the cases r and $r+\frac{1}{2}$ separately.

Case (*i*)—*Spin r* (*integral*).—For the representation (13, a), the (λ)-set is given by the scheme

$$(\lambda) = (r, r, \ldots r;\ \overline{r-1}, \ldots, \overline{r-1};\ \ldots;\ 1, \ldots 1;\ 0, \ldots 0) \qquad (16\cdot1)$$

the successive integers being repeated $(k-i_1)$, $(i_1-i_2), \ldots, i_r$ times respectively. Therefore the (l)-set is given by the scheme

$$(l) = (k+r-1, \ldots, i_1+r;\ i_1+r-2, \ldots, i_2+r-1;\ i_2+r-3, \ldots 1, 0) \qquad (17\cdot1)$$

(*a*) $n = 2k + 1$.—We use (6, *a*), and introduce in the sequence l_p' the missing terms $(i_1 + r - \frac{1}{2})$, $(i_2 + r - \frac{3}{2}), \ldots$ while forming the product $\Pi (l_p'^2 - l_q'^2)$, and then divide by the additional factors thus introduced. This gives, after some easy simplification, the order of the representation as

$$d_{i_1 i_2, \ldots i_r} = \frac{\prod_{p=1}^{r} (2k + 2r - 2p + 1)! \; \Delta_{p=1}^{r} \{(i_p + r - p + \frac{1}{2})^2\}}{\prod_{p=1}^{r} (k - i_p + p - 1)! \; \prod_{p=1}^{r} (k + i_p + 2r - p)!} \qquad (18, a)$$

where Δ will be used hereafter to denote the difference product. We can transform (18, *a*) to an elegant determinantal form by writing

$$(i_p + r - p + \tfrac{1}{2}) - (i_q + r - q + \tfrac{1}{2}) = (k - i_q + q - 1) - (k - i_p + p - 1)$$

and,

$$(i_p + r - p + \tfrac{1}{2}) + (i_q + r - q + \tfrac{1}{2}) = (k + i_q + 2r - q) - (k - i_p + p - 1)$$

and reducing it to a form in which there are only products of factorial expressions both in the numerator and denominator. This reduction gives

$$d_{i_1 i_2 \ldots i_r} = \begin{vmatrix} \binom{2k + 2r - 1}{k - i_1}, \binom{2k + 2r - 1}{k - i_2 + 1}, \ldots \binom{2k + 2r - 1}{k - i_r + r - 1} \\ \binom{2k + 2r - 3}{k - i_1 - 1}, \binom{2k + 2r - 3}{k - i_2}, \ldots \binom{2k + 2r - 3}{k - i_r + r - 2} \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \binom{2k + 1}{k - i_1 - r + 1}, \binom{2k + 1}{k - i_2 - r + 2}, \ldots \binom{2k + 1}{k - i_r} \end{vmatrix} \qquad (19, a)$$

which is a determinant of the r-th order. In the abbreviated form $| a_{pq} |$ of a determinant the element in the p-th row and q-th column of which is a_{pq} we can write

$$d_{i_1 \ldots i_r} = \left| \binom{2k + 2r - 2p + 1}{k - i_q + q - p} \right| \qquad (20, a)$$

(*b*) $n = 2k$.—We use the same (λ) and (l)-sets as in (15, *a*) and (17, *a*), but the second formula of (6, *b*) since $l_k = 0$. This gives

$$d_{i_1 i_2 \ldots i_r} = \frac{\prod_{p=1}^{r} (2k + 2r - 2p)! \; \Delta_{p=1}^{r} \{(i_p + r - p)^2\}}{\prod_{p=1}^{r} (k - i_p + p - 1)! \; \prod_{p=1}^{r} (k + i_p + 2r - p - 1)!} \qquad (18, b)$$

or in the determinantal form

$$d_{i_1 i_2 \ldots i_r} = \begin{vmatrix} \binom{2k+2r-2}{k-i_1}, \binom{2k+2r-2}{k-i_2+1}, \ldots \binom{2k+2r-2}{k-i_r+r-1} \\ \binom{2k+2r-4}{k-i_1-1}, \binom{2k+2r-4}{k-i_2}, \ldots \binom{2k+2r-4}{k-i_r+r-2} \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \binom{2k}{k-i_1-r+1}, \binom{2k}{k-i_2-r+2}, \binom{2k}{k-i_r} \end{vmatrix} \quad (19, b)$$

a determinant again of order r which can be abbreviated as

$$d_{i_1 i_2 \ldots i_r} = \left| \binom{2k+2r-2p}{k-i_q+q-p} \right| \quad (20, b)$$

Case (*ii*).—*Spin* $(r+\frac{1}{2})$ (*half-integral*)—For the representation (13, *b*) the (λ)-set is given by

$$(\lambda) = (r+\tfrac{1}{2}, \ldots, r+\tfrac{1}{2};\ r-\tfrac{1}{2}, \ldots, r-\tfrac{1}{2};\ \ldots;\ \tfrac{3}{2}, \ldots, \tfrac{3}{2};\ \tfrac{1}{2}, \ldots, \tfrac{1}{2}) \quad (16{\cdot}2)$$

the successive half-integers $(r+\frac{1}{2})$, $(r-\frac{1}{2}), \ldots, \frac{1}{2}$ being repeated $(k-i_1)$, $(i_1-i_2), \ldots, i_r$ times respectively. Therefore from (7) the (l)-set is given by

$$(l) = (k+r-\tfrac{1}{2}, \ldots, i_1+r+\tfrac{1}{2};\ i_1+r-\tfrac{3}{2}, \ldots, i_2+r-\tfrac{1}{2};\ i_2+r-\tfrac{5}{2}, \ldots, \tfrac{5}{2}, \tfrac{1}{2}) \quad (17{\cdot}2)$$

(*a*) $n = 2k+1$.—We use (6, *a*) and proceed as in the case of integral spin to derive

$$d_{i_1 \ldots i_r} = 2^k \frac{\prod_{p=1}^{r} (2k+2r-2p+1)! \ \Delta_{p=1}^{r} \{(i_p+r-p+1)^2\} \ \prod_{p=1}^{r} (2i_p+2r-2p+2)!}{\prod_{p=1}^{r} (k-i_p+p-1)! \ \prod_{p=1}^{r} (k+i_p+2r-p+1)!} \quad (21, a)$$

Comparing this with (18, *a*) we notice that (21, *a*) has an additional factor appearing in the numerator, and in the transformation to the determinantal form we also use

$$(2i_p + 2r - 2p + 2) = (k + i_p + 2r - p + 1) - (k - i_p + p - 1),$$

and this leads from (21, *a*) to the expression

$$d_{i_1 i_2 \ldots i_r} = 2^k \Sigma \pm \left| \binom{2k+2r-2p+1}{k-i_q+q-p} \right| \quad (22, a)$$

The 2^r determinants in the summation in (22, *a*) are derived from (20, *a*) by diminishing the indices $i_1, i_2, \ldots, i_r$ by one, one at a time, two at a a time, and to on, and attaching the $\pm$ sign according as the number of indices decreased by one be even or odd respectively. In other words, the several determinants in (22, *a*) are derived from (20, *a*) by diminishing by

one the expression $(k - i_q + q - p)$ in one column, two columns, and so on at a time. It might be observed that the summation in (22, *a*) is analogous to that on the right-hand side of (5).

(*b*) $n = 2k$.—The (λ) and (l)-sets are the same as in (16·2) and (17·2) but we use the first formula of (6, *b*) since $l_k \neq 0$. This gives

$$d_{i_1 \ldots i_r} = 2^k \frac{\prod_{p=1}^{r} (2k+2r-2p)! \; \Delta_{p=1}^{r} \{(i_p+r-p+\frac{1}{2})^2\} \; \prod_{p=1}^{r} (2i_p+2r-2p+1)!}{\prod_{p=1}^{r} (k-i_p+p-1)! \; \prod_{p=1}^{r} (k+i_p+2r-p)!} \quad (21, b)$$

In terms of determinants this reduces just like (22, *a*) to

$$d_{i_1 i_2 \ldots i_r} = 2^k \Sigma \pm \left| \binom{2k+2r-2p}{k-i_q+q-p} \right| \quad (22, b)$$

The orders of the several representations given by (20) and (22) can be expressed in terms of s by using (8).

5. Discussion of Results

The representations of the highest order are given by setting $i_1 = i_2 = \ldots = i_r = 0$ in the fromulæ of the previous section. We shall denote these by $d^{(r,s)}_{\max}$, and derive the relation between $d^{(r,s-1)}_{\max}$ and $d^{(r,s)}_{\max}$ when s is odd. From (18, *b*)

$$d^{(r,s)}_{\max} = \frac{\Pi \; (2k+2r-2p)! \; \{\Delta \; (r-p)^2\}}{\Pi \; (k+p-1)! \; \Pi \; (k+2r-p-1)!}$$

Again, from (18, *a*), putting $i_p = 0$, and changing k into $(k-1)$

$$d^{(r,s-1)}_{\max} = \frac{\Pi \; (2k+2r-2p-1)! \; \Delta \; \{(r-p+\frac{1}{2})^2\}}{\Pi \; (k+p-2)! \; \Pi \; (k+2r-p-1)!}$$

Now,

$$\Delta \; \{(r-p)^2\} = (r-1)! \prod_{1}^{(r-1)} (2r-2p-1)!$$

and

$$\Delta \; \{(r-p+\tfrac{1}{2})^2\} = \prod_{1}^{(r-1)} (2r-2p)!$$

Hence

$$\frac{d^{(r,s)}_{\max}}{d^{(r,s-1)}_{\max}} = \frac{\Pi \; (2k+2r-2p) \cdot (r-1)!}{\Pi \; (k+p-1) \prod_{1}^{(r-1)} (2r-2p)} = 2^r \cdot \frac{(r-1)!}{2^{r-1} (r-1)!} = 2$$

Thus,

$$d^{(r,s-1)}_{\max} = \tfrac{1}{2} \, d^{(r,s)}_{\max} \quad (23, a)$$

In general, therefore, the order of each of the twin representations for odd s is equal to that of the highest order reprsenetation for $(s-1)$. In a similar way, using (21, a) and (21, b) we can show that for $n = 2k$ (s odd)

$$d_{\max}^{(r+\frac{1}{2},\, s-1)} = \tfrac{1}{2}\, d_{\max}^{(r+\frac{1}{2},\, 's)} \qquad (23, b)$$

A simpler proof is also possible using (20, a) and (20, b).

For the usual case of four elements β_μ, *i.e.*, $s = 4$, formulæ (18, a) and (21, a) give the dimensions of the representations for spins r and $r + \frac{1}{2}$ by putting $k = 2$. Considering (18, a) first, let us take the choice of indices given by

$$i_1 = i_2 + \ldots = i_j = 1\,;\; i_{j+1} = \ldots = i_r = 0 \qquad (24)$$

This gives after some simplification

$$d_{(1)^j\,(0)^{r-j}} = \tfrac{1}{6}\,(2r+3)\,(j+1)\,(2r-2j+1)\,(2r-j+2)$$

Changing j into $(r-j)$, this gives

$$d_{(1)^{r-j}\,(0)^j} = \tfrac{1}{6}\,(2r+3)\,(r-j+1)\,(2j+1)\,(r+j+2) \qquad (25)$$

We can replace in this r and j by the indices λ_1, λ_2 and the general representation for spin λ_1 characterised by (λ_1, λ_2) where λ_2 takes on values from 0 to λ_1, has therefore the dimension

$$\begin{aligned} d_{(\lambda_1,\,\lambda_2)} &= \tfrac{1}{6}\,(2\lambda_1+3)\,(\lambda_1-\lambda_2+1)\,(2\lambda_2+1)\,(\lambda_1+\lambda_2+2) \\ &= \tfrac{2}{3}\,(\lambda_1+\tfrac{3}{2})\,(\lambda_2+\tfrac{1}{2})\,(\lambda_1-\lambda_2+1)\,(\lambda_1+\lambda_2+2) \end{aligned} \qquad (26)$$

which is identical with the formula in M. p. 314 for the case $n = 5$, $k = 2$. It can be shown that the substitution (24) in (21, a) also leads to the same formula (26) with $\lambda_1 = r + \frac{1}{2}$, $\lambda_2 = j$.

6. Summary

It is shown that the results obtained by Schrödinger, and Kemmer for the s-element meson algebra also hold for the generalisation, to s elements, of the algebra corresponding to general spins r and $(r + \frac{1}{2})$ previously set up by the author. The representations of this algebra are obtained by analysing the direct product of the basic representation of the rotation group of $(s+1)$ dimensions with itself taken $2r$ or $2r+1$ times. The total number of representations (excluding those belonging to lower spins) is obtained as $(k+r-1)\,C_r$ or $(k+r-1)\,C_r + 1$ for $n = s+1 = 2k+1$ or $2k$ respectively, both for spins r and $(r+\frac{1}{2})$. The order of a general representation specified by r indices $i_1, i_2, \ldots, i_r$ is given in a simple determinantal form in the four cases of $n = 2k+1$ or $2k$, and spins r or $(r+\frac{1}{2})$. It is also shown in general that the twin representation for odd s has the same order as that of the highest one for $(s-1)$ elements.

The method of the paper leads to an alternative derivation of Kemmer's results for the meson case, and to equally simple results for the generalised s-element algebra of spin $\frac{s}{2}$.

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COLOURING MATTER OF TAMBUL SEEDS

Part IV. Synthesis of Tambuletin

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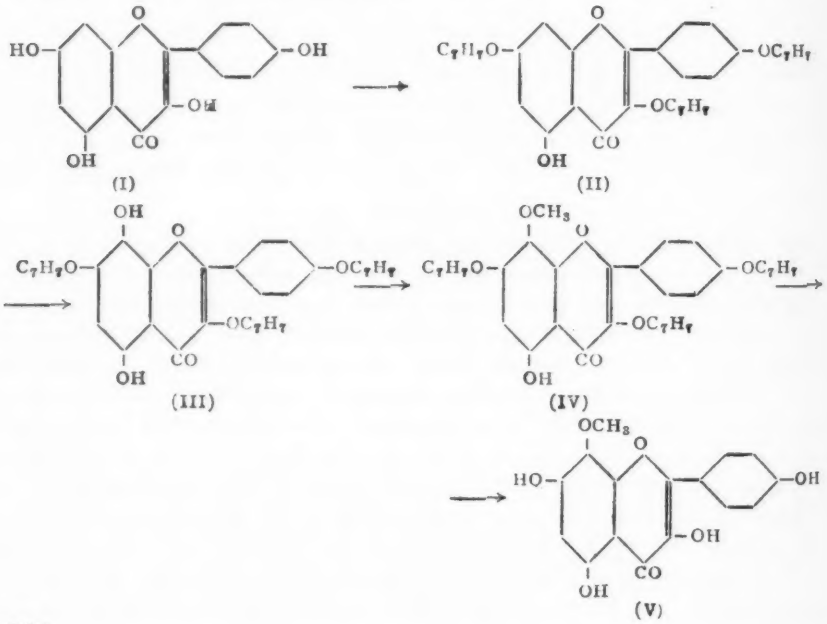
Received July 15, 1947

From a consideration of the properties and reactions of tambuletin, it was given the constitution of the 8-methyl-ether of herbacetin.[1] This constitution was subsequently confirmed[2] by the preparation of its tri- and tetra-ethyl ethers and by their identity with 3:7:4′-triethoxy-8-methoxy-5-hydroxy flavone and 3:5:7:4′-tetraethoxy-8-methoxy flavone respectively. The synthesis of tambuletin itself has now been achieved and is reported in this paper.

The synthetic preparation of tambuletin follows on lines similar to the synthesis of wogonin[3] from chrysin. Starting with kæmpferol (I) it is subjected to partial benzylation using three molecular proportions of benzyl



chloride. The product should be 3:7:4′-O-tribenzyl-ether (II) having the resistant 5-hydroxyl free. This constitution is supported by its properties since it gives a strong ferric chloride colour and is sparingly soluble in aqueous alkali. Its oxidation to the quinol (III) takes place with some difficulty owing to its sparing solubility in alkali even in the presence of pyridine and only poor yields are obtained. Partial methylation of this quinol yields the 8-methyl ether (IV) which gives the reactions for a free 5-hydroxyl. Final debenzylation takes place smoothly producing 8-methoxy-3:5:7:4′-tetrahydroxy-flavone (V) which is found to be identical in all respects with tambuletin isolated from tambul seeds.[1]

Experimental

5-Hydroxy-3:7:4′-tribenzyloxy-flavone (II)

Kæmpferol (I) (1·0 g.) was dissolved in dry acetone (50 c.c.) and anhydrous potassium carbonate (8·0 g.) and benzyl chloride (1·13 c.c., 3 mols.) were added. The mixture was refluxed for 20 hours. The potassium salts were filtered off and washed with hot acetone. The filtrate was concentrated on a water-bath as far as possible and the residue stirred up with water. A semi-solid separated out. It crystallised from a mixture of alcohol and acetone as pale yellow small prisms melting at 111–13° (Found: C, 78·0; H, 5·0; $C_{36}H_{28}O_6$ requires C, 77·7; H, 5·0%). It gave a green colour with alcoholic ferric chloride and was sparingly soluble in aqueous alkali.

5:8-Dihydroxy-3:7:4′-tribenzyloxy-flavone (III)

The 5-hydroxy compound (II) (1·7 g.) was dissolved in pyridine (50 c.c.) and an aqueous solution of sodium hydroxide (1·0 g. in 20 c.c. of water) was added. The mixture was stirred for 2 hours while an aqueous solution of potassium persulphate (2·0 g. in 40 c.c. of water) was added gradually drop by drop. The solution was kept aside overnight and acidified to congo red with hydrochloric acid. The unreacted compound was filtered off and the filtrate extracted twice with ether to remove the last traces of it. Sodium sulphite (3·0 g.) and concentrated hydrochloric acid (20 c.c.) were added to the aqueous solution which was then heated over a boiling water-bath for 30 minutes. After cooling the solution, the soild that had separated out was extracted with ether. Removal of ether by distillation left a bright yellow substance. It crystallised from alcohol in the form of bright yellow narrow rectangular plates and flat needles melting at 165–66° (Found: C, 75·3; H, 5·0; $C_{36}H_{28}O_7$ requires C, 75·5; H, 4·9%). It gave a transient green colour changing to brown with alcoholic ferric chloride and was soluble in aqueous alkali producing a reddish-brown solution.

5-Hydroxy-8-methoxy-3 : 7 : 4′-tribenzyloxy-flavone (IV)

The 5 : 8-dihydroxy compound (III) (0·8 g.) was dissolved in dry acetone (25 c.c.) and anhydrous potassium carbonate (5·0 g.) and dimethyl sulphate (0·14 c.c., 1 mol.) were added. The mixture was refluxed for 6 hours. The potassium salts were filtered off and washed with hot acetone. The filtrate was concentrated over a water-bath to remove acetone. The solid that remained behind was stirred up with water and filtered. It crystallised from a mixture of alcohol and acetone as pale yellow prismatic needles melting at 113–15° (Found: C, 75·5; H, 5·0; $C_{37}H_{30}O_7$ requires C, 75·8; H, 5·1%). It gave a green colour with alcoholic ferric chloride and was sparingly soluble in aqueous alkali.

8-Methoxy-5 : 7 : 3 : 4′-tetrahydroxy-flavone (V) (Tambuletin)

The above 5-hydroxy compound (0·5 g.) was treated with a mixture of glacial acetic acid (5·0 c.c.) and concentrated hydrochloric acid (2·5 c.c.) and the mixture was heated at 100° over a water-bath for one hour. The solution was cooled and diluted with water. A bright yellow solid separated out. It was filtered and crystallised from glacial acetic acid whereby it was obtained as bright yellow short needles melting at 269–70°. It gave a dull green colour with alcoholic ferric chloride and was readily soluble in aqueous alkali to give a bright yellow solution. It gave an orange-red precipitate with neutral lead acetate in alcohol. The mixed melting point with a sample of tambuletin isolated from the seeds of *Zanthoxylum acanthopodium* was not depressed (Found: C, 60·3; H, 4·0; $C_{16}H_{12}O_7$ requires C, 60·7; H, 3·8%).

SUMMARY

The synthesis of tambuletin has been effected. Kæmpferol is first benzylated to the tribenzyl-ether which is subjected to oxidation with alkaline persulphate, partial methylation and debenzylation in succession.

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ERRATUM

In Part III, A, 1947, **26**, 216 *read* (VIII), *for* (XIII) at the bottom of the page.

STUDIES IN CHARNOCKITES FROM ST. THOMAS MOUNT, MADRAS—PART II*

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Received February 14, 1947
(Communicated by Prof. C. Mahadevan, F.A.SC.)

Introduction

In a recent contribution by the author (Part I) on the above subject, the mineralogy of the charnockites from St. Thomas Mt. was detailed. In this part the petrology and the petrogenesis of the series are given.

General Characters

The rocks of this series are in general blue grey or darkish in colour with a remarkably fresh appearance and an even-grained granulitic texture. They range from a highly siliceous hypersthene-granite through diorites and norites to pyroxenites. An examination with a lens shows that plagioclase and quartz when present are almost invariably blue or bluish green, while the alkali felspars show a definite tinge of green. These dark shades of the salic minerals, with the large abundance of femic minerals, give the same dark appearance to all the members of the series, acid, as well as basic.

Under the microscope the minerals show a remarkable constancy in their essential optical properties, in all the types. In texture, the rocks are typically even-grained and granulitic while in mineral composition there is a constant presence of pleochroic rhombic pyroxene. The other femic minerals which make up the rocks of this series are augite and hornblende, while the opaque iron ores in minute grains are universally present. The salic minerals are plagioclase felspars, alkali felspars and quartz. A character which is often observed in the rocks is the tendency of the femic minerals to cluster together, a feature which was also noted by Holland (1900 B, p. 118).

In the present collection six types could be distinguished, whose chemical analyses, norm, etc., are given in Table I.

* For Part I, see this Journal, Vol. XXIV, No. 4, Sec. A, pp. 315-331, 1946.

TABLE I

Chemical analyses of charnockites from St. Thomas Mount, Madras

	A	B	C	D	E	F
SiO_2 ..	49·05	50·09	52·72	69·35	71·73	74·99
Al_2O_3 ..	12·82	16·52	16·64	14·66	14·76	13·21
Fe_2O_3 ..	2·76	1·97	0·78	1·40	1·05	0·03
FeO ..	14·50	11·35	11·34	4·64	1·34	1·99
MnO ..	0·35	0·45	0·45	0·06	0·08	0·12
MgO ..	4·55	5·88	4·24	1·98	0·44	1·05
CaO ..	10·06	9·03	8·89	2·34	2·62	1·09
Na_2O ..	3·12	2·64	3·50	4·26	4·46	3·51
K_2O ..	0·91	0·51	0·57	0·83	3·28	3·19
TiO_2 ..	2·01	1·49	1·02	0·74	0·62	1·09
P_2O_5 ..	0·36	0·35	0·36	Trace	..	..
H_2O+ ..	..	..	..	0·03	0·04	0·19
H_2O- ..	0·09	0·06	0·07	0·33	0·05	0·13
Total ..	100·58	100·44	100·52	100·62	100·47	100·59
Sp. Gr. ..	3·12	3·16	3·00	2·77	2·67	2·70
			NIGGLI VALUES			
si ..	113	117	133	291	350	425
al ..	17	23	25	36	42	44
fm ..	50	48	42	33	13	19
c ..	25	23	24	11	13	7
alk ..	8	6	9	20	32	30
k ..	0·17	0·10	0·08	0·12	0·33	0·38
mg ..	0·32	0·43	0·38	0·38	0·25	0·47
			BASIS COMPOSITION			
Kp ..	3·4	1·7	1·7	3·1	11·7	11·5
Ne ..	17·1	14·4	18·8	23·2	24·0	18·9
Cal ..	11·1	19·2	17·1	7·1	6·3	3·4
Cs ..	8·3	2·5	3·3	..	0·7	..
Fs ..	3·1	2·2	0·8	1·5	1·2	..
Fa ..	17·6	14·0	13·8	5·4	1·6	2·4
Fo ..	9·8	12·5	8·9	2·2	0·9	0·6
Cp ..	1·4	1·3	1·3	..	..	..
Q ..	26·8	31·1	33·5	53·1	53·2	59·3
Ru ..	1·4	1·1	0·7	0·5	0·4	0·8
Sp ..	..	..	..	4·0	..	3·2
			C.I.P.W. NORM			
Q ..	..	..	0·96	30·42	27·30	37·74
Or ..	5·56	2·78	2·72	5·00	19·46	18·90
Ab ..	26·20	22·53	29·34	36·15	37·73	29·34
An ..	18·07	31·69	28·36	11·68	10·56	5·56
Hy { Mg ..	2·50	12·70	8·70	5·00	0·50	2·60
Hy { Fe ..	5·02	15·31	15·71	6·20	0·26	1·98
Ol { Fo ..	3·08	..	..	..	..	..
Ol { Fa ..	6·73	..	..	..	..	..
Di { Ca ..	12·18	4·41	5·45	..	0·93	..
Di { Mg ..	4·50	2·00	1·90	..	0·50	..
Di { Fe ..	7·92	2·38	3·70	..	0·26	..
Ap ..	1·01	1·01	1·01	..	..	..
Mt ..	4·18	3·02	1·16	2·09	1·62	..
Il ..	3·80	2·89	1·98	1·37	1·22	2·13
C ..	..	..	..	2·45	..	1·94

TABLE I—(*Contd.*)

	A	B	C	D	E	F
KATA MOLECULAR NORM						
Q ..	..	..	0·4	26·0	27·1	32·9
Or ..	5·7	2·8	2·8	5·2	19·5	19·2
Ab ..	28·5	24·0	31·3	38·7	40·0	31·5
An ..	18·5	31·8	28·5	11·8	8·4	5·7
Wo ..	8·3	1·1	3·0	..	0·1	..
Hy ..	11·2	16·4	17·9	6·1	1·3	3·2
En ..	6·8	15·6	11·9	2·9	1·2	0·8
Fo ..	4·7	0·8	..	..	..	..
Fa ..	7·6	0·6	..	..	..	..
Ap ..	1·4	1·3	1·3	..	..	..
Tn ..	4·2	3·3	2·1	..	1·2	..
Ru ..	..	..	..	0·5	..	0·8
Mt ..	3·1	2·2	0·8	1·5	1·2	..
Cord ..	..	..	..	7·3	..	5·9
MODE						
Qz ..	..	..	4·4	36·0	26·7	34·1
Alkali-felspar (Perthite)	..	..	4·1	13·2	48·5	42·8
Plagioclase ..	49·1	51·0	49·5	34·6	20·2	15·8
R. Px ..	12·2	10·2	16·2	13·7	2·6	6·1
M. Px ..	8·5	26·1	13·9	(mostly hypersthene)	..	..
Hornblende ..	28·9	2·1	1·3	..	..	..
"Ores" ..	0·3	9·4	9·4	2·5	2·0	1·2
Apatite ..	1·0	1·2	1·2	..	..	..

A. Hornblende Norite (Melagabbrodiorite) (III. 5. 4. 4.) sp. No. M St/53. St. Thomas Mount, Madras, Analyst.—C. Rajagopalan.

B. Hy-Gabbro (Normal gabbroid) (III. 5. 4. 5.) sp. No. M St/33. Same locality as A, Analyst.—C. Rajagopalan.

C. Norite (Orbitisch) (III. 5. 4. 5.) sp. No. M St/23. Locality same as above. Analyst.—C. Rajagopalan.

D. Granodiorite (Moyitisch) (II. 4. 2. 5.) sp. No. M St/38. Locality same as above. Analyst.—C. Rajagopalan.

E. Granite (Yosemitgranitisch) (I. 4. 2. 4.) sp. No. M St/29. Locality same as above. Analyst.—C. Rajagopalan.

F. Hypersthene-granite (Natronrapakawitisch or Rapakawitisch) (I. 3. 2. 3.) sp. No. M St/56. Locality same as above. Analyst.—C. Rajagopalan.

DESCRIPTION OF THE CHIEF TYPES

In the petrographic description the megascopic features are omitted since all the types look more or less similar.

Hornblende-Norite (Melagabbrodiortisch) Type A.—This is the most important member of this series and appears to have, as explained further

below, the same composition as of the probable "parent magma" of the charnockite suite. It is a dark green medium grained rock made up of, as seen microscopically, plagioclase, hornblende and pyroxene with a little of apatite and opaque iron ores. Hornblende, the abundant of the femic constituents, is seen disposed in bands, markedly parallel with pyroxene and felspars.

The modal felspar of this rock is about 49% while the normative quantity varies from 50% to 53%. This slight deficiency in the modal felspar is probably due to the hornblende taking up some amount of alkalies and lime (*vide* Part I). The plagioclase according to the norm will approximately have an anorthite content of about 40% which agrees fairly well with the determination on the universal stage (*vide* Part I).

Hypersthene-Gabbro (Normal gabbroid) Type B.—Under the microscope, the plagioclase, mostly twinned, is found to constitute about 50% of the bulk. Pyroxenes of which the monoclinic is the most abundant, makes up nearly 35%, while hornblende is present in small quantities. Accessory magnetite, pyrite are abundant. Quartz is present only in very small quantities.

On examining the mode and the norm it is seen that there is orthoclase in the norm and none at all in the mode. This is probably due to its solid solution in plagioclase. Universal stage determination gives an anorthite content of 45% to the plagioclases, which nearly corresponds to that derived from the Norm.

Norite (Orbitisch) Type C.—This is a dark grey fine grained rock sometimes showing fairly large crystals of the femic minerals.

Under the microscope it is typically fresh. The plagioclase constitutes 45% of the volume. Rhombic pyroxene predominates over the monoclinic. Hornblende and apatite are present in small amounts, while opaque iron ores make up more than 9% of the bulk. A little alkali felspar is also present.

On comparing the mode with the norm it is seen that the alkali felspar is probably a perthite of the composition Or_2 Ab_1. The resulting plagioclase would then correspond to Ab_1 An_1 agreeing nearly with the determinations on the universal stage (*vide* Part I).

Granodiorite (Moyitisch) Type D.—In thin sections under the microscope the quartz is seen to be abundant. But the small quantity of hardly 13% of the alkali felspars, a plagioclase which is rather basic, considerable amounts of hypersthene with some monoclinic pyroxene and apatite point out that this has basic affinity.

It is seen from the Table I that there is an excess of modal quartz over the normative. This discrepancy may be due to untwinned felspar pieces having been counted with quartz. The 13% of modal alkali felspars against only of about 5% normative means that it is a micro-perthite of approximately Or_2 Ab_3. The resulting plagioclase will, hence, have an anorthite content of about 30% which very well agrees with the determination on the universal stage (*vide* Part I).

Granite (Yosemitgranitisch) Type E.—Magascopically the rock is a medium-fine grained one with dark greenish-grey colour and almost a greasy lustre.

Under the microscope it shows an abundance of quartz. Most of the felspar that is present is the alkali variety, some plagioclase, twinned and un-twinned, being also present. Subordinate amounts of hypersthene occurs with small quantities of magnetite and pyrite.

There is a good agreement between the normative and modal quartz and also total felspars. Whereas there is only 20% of plagioclase and 48½% of microcline, the normative quantities of orthoclase, albite and anorthite are 19½, 40 and 8½ respectively. It is therefore, very probable that micro-perthite of nearly Or_2 Ab_3 composition is observed as microcline. The resulting plagioclase will thus have an anorthite content of 40%.

Hypersthene-Granite (Natron-rapakawitisch or Rapakawitisch) Type F.—The rock, as seen in thin sections, is made up of felspars and quartz with a small amount of hypersthene and opaque iron ore and an occasional flake of biotite. The felspars include microcline and micro-perthite, the plagioclase being an acid oligoclase with an anorthite content of approximately 12%. Hypersthene tends to cluster together and shows some alteration.

From Table I it will be seen that in the Norm, corundum or cordiorite appears which shows there is an excess of alumina over the requirements of the combined alkalies and lime, indicating the presence of an aluminous mineral; also that the calculated quartz is more. This excess of normative alumina and quartz is very probably due to the hypersthene which, as has already been shown (*vide* Part I) is an aluminous and siliceous variety. The total felspars are more in the mode than in the Norm. The alkali felspars are nearly as much as the combined amount of potash. Thus it is probable as suggested by Washington (1916, p. 325) that there are some anorthite molecules also in the alkali felspars which is seen as "microcline".

General Chemical Characters

From a knowledge of the chemical composition of the minerals present in a rock, and the chemical composition of the rock, it is easy to calculate the modal composition. Since the important femic minerals of the charnockites were analysed, which were given in the previous part and since the composition of the plagioclase was also determined to a degree of accuracy that the Universal Stage permits, an attempt has been made to allot the Basis Molecules of the rock to the various minerals present in as close a proportion as they occur in the minerals themselves, thus arriving at what could be termed as the " Calculated Mode ". In Table I the Modes of the rocks were given which represented the volume percentage. The values after converting into weight percentages are given in Table II along with the "Calculated Mode".

TABLE II

MODE (Weight Percentage)

	A	B	C	D	E	F
Quartz ..	..	..	4	35	26½	34
Alkali felspars ..	..	..	4	12	47½	41
Plagioclase felspars ..	43½	43	42	31	20	15
Hypersthene ..	14	11	18	17	3	8
Augite ..	10	28	15		..	..
Hornblende ..	31	2	1	..	..	..
" Ores " ..	½	15	15	5	3	2
Apatite ..	1	1	1	..	..	..
CALCULATED MODE						
Quartz ..	..	..	4	30	24	34
Alkali felspars ..	..	..	54	15	48	31
Plagioclase felspars ..	40	48		35	21	24
Hypersthene ..	16	11	20	20	7	11
Augite ..	19	26	13	..	..	..
Hornblende ..	24	14	8	..	..	..
Apatite ..	1	1	1	..	..	..
" Ores " ..	..	..	..	..	..	..

A perusal of the observed and the claculated mode shows that there are certain apparent discrepancies in spite of the fact that no assumptions were made in the calculation of the mode, excepting, that there is a constancy in the chemical composition of the ferromagnesium minerals, *viz.*, augite, hypersthene and hornblende, in all the rock types. Though it could be argued that it is an unwarranted assumption, the optical properties of the above mentioned minerals are constant enough to believe that their chemical compostion is sensibly the same.

In rock type A, *i.e.*, Hornblende-Norite, all the calculated values for all the minerals except for augite and hornblende, agree fairly well. Whereas

the calculated augite is more than the observed one, the same for hornblende is correspondingly less. Hence it appears probable that at least part of the hornblende is derived from augite.

In rock type B and C the calculated values for hornblende are much higher than the observed ones, on the other hand " Ores " are abundant in the observed mode and none at all in the calculated one. It, therefore, appears probable that the " Ores " are mostly derived from hornblende. In other rock types there is a tolerably good agreement between the observed and the calculated modal values except for the felspar values of type F, which was already explained under the head hypersthene-granite.

Thus, from a chemical study supported by optical observations of the charnockites we find that the monoclinic pyroxene under certain conditions changes into hornblende which in its turn gives opaque iron ores; all these changes have obviously taken place without in any away affecting the fresh appearance of the rocks.

This series shows a very wide range in silica content from 75% to 49%. Alumina is usually low and is not more than enough to satisfy the combined alkalies and lime. Iron oxides are high and count for the abundant femic minerals. The ferrous oxide greatly predominates over the ferric. Manganese is very low as is quite normal to igneous rocks. Magnesia is always lower than the combined iron oxides. In the basic members lime is always in excess of alumina over alkalies, and is converted into normative diopside or wollastonite molecule, which enters into the composition of modal augite or hornblende. The alkalies are fairly high, soda largely predominating over potash, except in the most acid varieties where the amounts are almost equal. Titania, just like manganese is very low, but the amount increases in basic types. Phosphorus is totally absent in the acid members, and first shows its presence in the granodiorite and increases in the basic types, but never rises beyond 0·4%.

Petrochemistry

The chemical analyses of igneous rocks have been represented graphically differently by different authors. The most widely used methods now in the English-speaking countries is the one suggested by Harker. In this method either the oxide composition or the molecular proportions of the various oxides are plotted against SiO_2. Thus, to represent a petrographic province or a number of igneous rock types which are apparently of the same parentage there will be a graph with as many curves as there are oxides in the chemical composition. On the Continent, however, the chemical analyses are mostly interpreted, at any rate were interpreted until the beginning

of the World War II, on the lines initiated by Niggli. In this method instead of the weight percentages the important Niggli Values, *viz.*, *al*, *fm*, *c* and *alk* are plotted against *si* values. The values thus used bring about the variation of all the oxides which make up the principle rock forming minerals. Thus, the number of curves are reduced to four without in any way suppressing the character of the represented rock analyses, so that any serial variation could be more advantageously brought out and the variation in the values of *al*, *fm*, *c* and *alk* for differing values of *si* studied. Such a diagram is known as Niggli's Molecular Diagram or Differentiation Diagram for reasons which

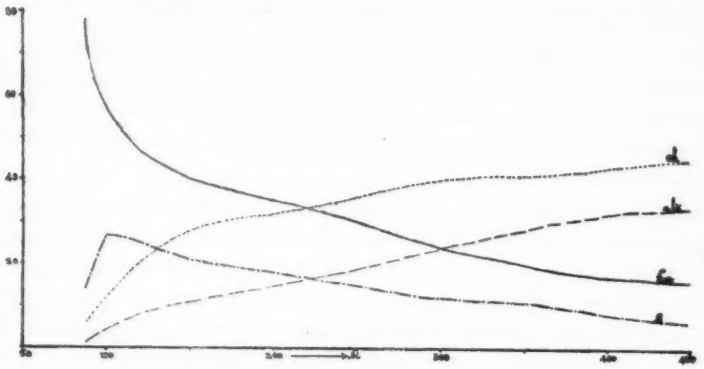

FIG. 1. Differentiation Diagram of the Charnockite Series

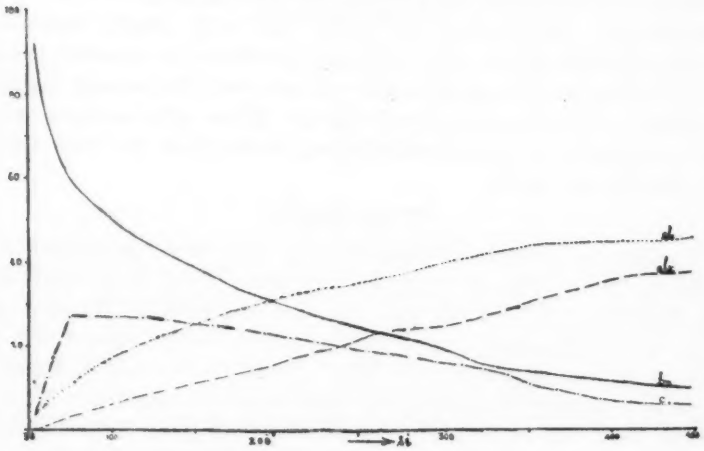

FIG. 2. Differentiation Diagram of the Cale-alkali Series (After Niggli (Reproduced from Burri, 1926, p. 137)

will be apparent in the following pages. It is a well recognised fact that there are at least two different tendencies of differentiation namely (1) the Calc-alkaline, or sub-alkaline and (2) the Alkaline. These two different tendencies of differentiation are very clearly brought out when the Niggli's Molecular Diagram is constructed and studied.

A differentiation diagram based on the above lines for the charnockites from the analyses given in Table I supplemented with those of nearby charnockites given by others such as Holland (1900) Washington (1916), Rama Rao (1945) is given in Fig. 1. For the sake of comparison a similar diagram for the calc-alkaline suite given by Niggli (Burri, 1926, p. 137) is reproduced in Fig. 2.

A consideration of Fig. 1 shows two sets of sympathetic curves, the *alk* being sympathetic to *al* and *c* to *fm*, while these two sets have mutually opposing tendencies. Thus, when *al* and *alk* increase *fm* and *c* fall and *vice versa*, except for very low values of *si* where *c* also shows an opposing tendency to *fm*. A striking feature of the diagram is the smoothness of the curves, without sharp rises and falls except for very low values of *si*.

The *fm* curve between the *si* values of 88 and 120 is very steep and the value changes very rapidly even for small variations of *si*. Later, there is a gradual decrease as *si* increases, without sudden fall in the values of *fm* until it attains a minimum value of 16 units when $si = 450$.

The *al* curve starting with a low value of 6 units when $si = 88$ fairly rapidly rises to 28 units at $si = 150$; then the values slowly but steadily increase until a maximum of 45 units is reached at $si = 450$.

The *c* curve has a very steep rise in the initial stages from a value of 15 units at $si = 88$ to 26 units at $si = 100$; then slowly decreases in value, being almost sympathetic to *fm*.

The *alk* on the other hand steadily increases in its values starting almost with a value of zero at $si = 88$ units and rising to 33 units at $si = 450$. This curve is thus sympathetic to *al* curve.

On a closer study of the two diagrams it will be seen that there is not merely a general similarity in the tendencies of the curves, but that the intersection point of *al* and *fm* curves is very nearly at the same *si* value. This point, known as the Isofalic point, gives an *si* value which is characteristic for each petrographic province. Thus, the Isofalic point for Circumpacific or Calc-alkaline rocks falls at $si = 180$ or more, while the same in the alkaline suites—both Atlantic and Mediterranian—rarely exceeds $si = 160$. This point in Fig. 1 falls at $si = 216$. Here the other values are $al = fm$

$= 33 \cdot 5$; $c = 17$, $alk = 16$. Thus strong affinity to calc-alkaline suite is clearly indicated by the charnockites. It will be shown further that similar tendencies are exhibited by the charnockites in other typical diagrams.

The interpolated values of the differentiation diagram of the charnockite is given in Table III.

TABLE III

si	*al*	*fm*	*c*	*alk*	*al-alk*	*c-(al-alk)*	*alk/al-alk*	*qz*
120	20	47	25	8	12	+13	0·67	−12
150	28	40	21	11	17	+ 4	0·65	+ 6
200	32	35	18	15	17	+ 1	0·88	+40
250	36	30	15	19	17	− 2	1·12	74
300	40	24	12	24	16	− 4	1·50	114
350	41	20	11	28	13	− 2	2·16	138
400	43	17	8	32	11	− 3	2·91	172
450	45	16	6	33	12	− 6	2·75	218

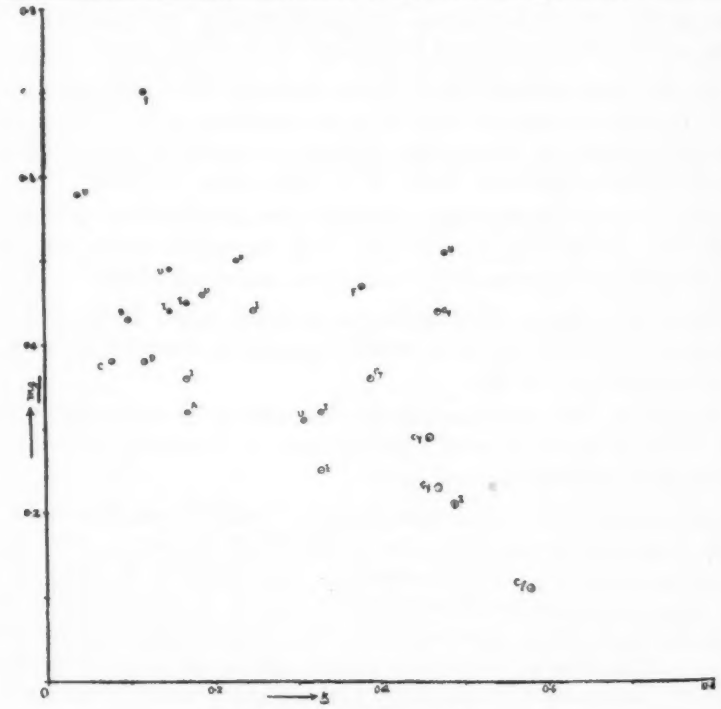

FIG. 3. *k-mg* Diagram
A to F = Authors Rocks U = Charnockites from Uganda
Cy = Charnockites from Ceylon I = „ „ India

The above table besides giving the interpolated values, also gives some idea of the normative mineral composition. Thus, when *al* is not more than (*c* — *alk*) then, (*al* — *alk*) gives an idea of the anorthite content of the rock. The value *c* — (*al* — *alk*) gives the proportion of lime which is not in combination with alumina but is available for ferromagnesian minerals, *i.e.*, normative wollastonite. The ratio *alk*/*al* — *alk* gives the proportion of alkali felspars over anorthite felspar. The value of free silica, *i.e.*, q^2 is given by *si* — (100 + 4 *alk*).

k — *mg* Diagram

The differentiation diagram of the charnockite-series studied above has its inherent drawbacks in that, the individual behaviour of the components soda and potash, iron and magnesia cannot be followed. This purpose is served by the *k* — *mg* Diagram given in Fig. 3.

From the diagram it will be seen that all the plotted points arrange themselves roughly in a North-west South-east zone. Thus, an increase in the values of *k* is accompanied by decrease in *mg* values and *vice versa*. This opposing tendency of these two are features characteristic of the Circum-pacific Suite.

Normative Mineral Diagram

It has already been pointed out how the normative mineral composition could be estimated from the Niggli values.

When there is enough of SiO_2 and when *al* is more than *alk*, but less than (*alk* + *c*) (which is normally the case) then, 2 *alk* gives the proportion of alkali felspars 2 (*al* — *alk*) a measure of the anorthite content and (100 — 2 *al*) the amount of dark minerals. The sum of these three quantities being hundred, could be projected by a single point in a trilinear diagram, the three values occupying the three corners of an equilateral triangle. These values for the six types given in Table IV, provide a very valuable basis for

Table IV

Type	2 *alk*	2(*al*-*alk*)	(100-2*al*)
A	16	18	66
B	12	34	54
C	18	32	50
D	40	32	28
E	64	20	16
F	60	28	12

following the differentiation trends. Thus it will be clear from Fig. 4 that the general sequence of events is to follow two distinct courses from a

common point A. Along one of the courses there is enrichment of the dark minerals with concomitant impoverishment in the total felspars resulting in the pyroxenite type. Along the other, the sequence is first impoverish-

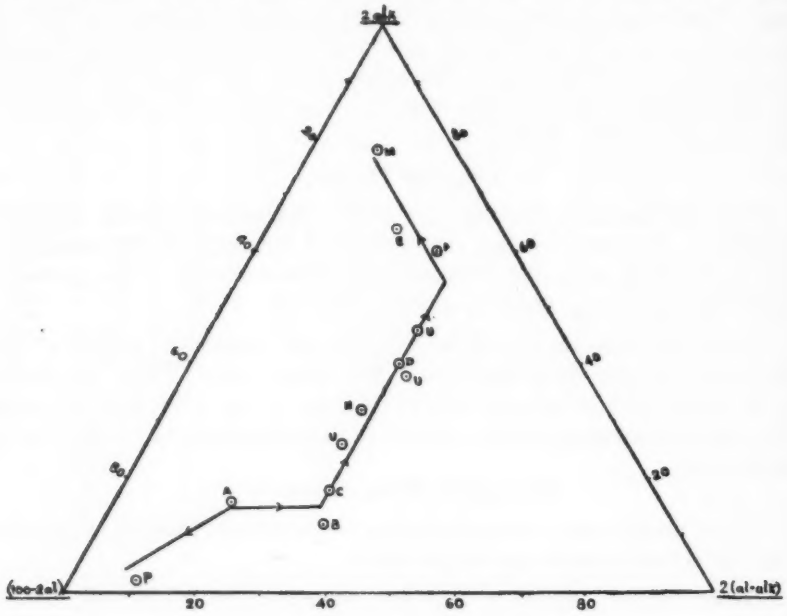

FIG. 4. Normative Mineral Diagram

ment in femic constituents with constant alkali felspars resulting in types B and C, secondly from there, enrichment in alkali felspars with constant anorthite content and from there impoverishing of anorthite molecule with constant femic constituents giving rise to more and more acid types like E, F and M.

Q-L-M. DIAGRAM

A study such as the above one is, however, based on the express assumption that silica was always available for the formation of the saturated minerals.

In view of the prime importance of silica in the formation of the rock types, it is necessary to study the behaviour of this important constituent also during the progress of differentiation. This is done with the help of the Q-L-M diagram (Fig. 5) where Q stands for Q of the Basis composition, L is equal to (Kp + Ne + Cal) and M embraces all the femic Basis Molecules. Thus, the composition of a rock could be expressed in three values

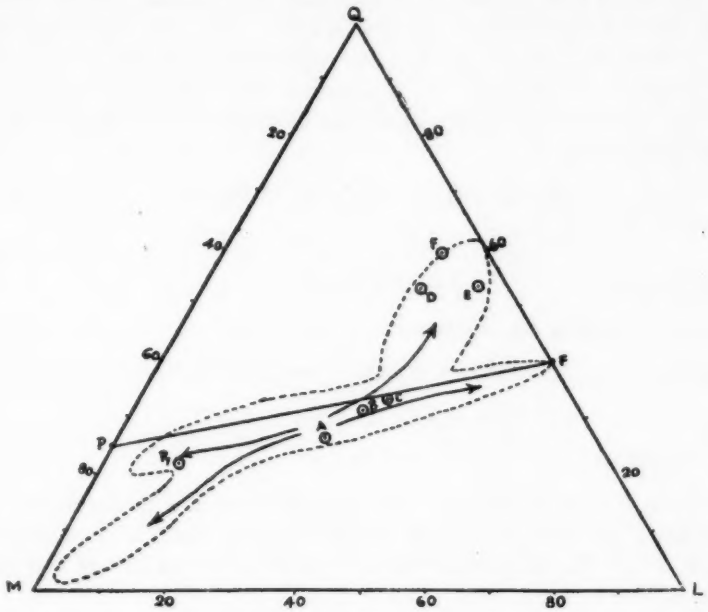

FIG. 5. Q. L. M. Diagram

Q, L & M (Table V.) M standing for the unsaturated melanocratic constituents, L standing for the unsaturated felspar molecules and Q for the

TABLE V

	A	B	C	D	E	F
Q ..	28·2	32·2	34·2	53·6	53·6	60·1
L ..	31·6	35·3	37·6	33·4	42·0	33·8
M ..	40·2	32·5	28·2	13·0	4·4	6·1

availability of SiO_2 for saturating the above two. Both the diagrams are apparently alike, but it will be seen that the diagram based on 2 *alk*, 2 (*al* − *alk*) and (100 − 2 *al*) gives the individual behaviour of the two felspars —the alkali and lime,—which in the Q-L-M diagram are blended into a single value L. This later diagram, on the other hand, gives the behaviour of SiO_2 during the whole progress of differentiation, which is lacking in the previous diagram. Thus, both of them are very useful in elucidating the trends of differentiation.

In the Q-L-M diagram it is seen that there are two points: (1) P on the side of Q-M and (2) F on the side of Q-L. These two points are the positions of the pyroxenes and felspars respectively. M (Fo + Fa + Fs + Cs) representing the position of unsaturated ferromagnesiam minerals, takes certain amount of Q for the formation of pyroxene according to the following equation:—

$$Mg\ Mg\ SiO_4 + SiO_2 \rightarrow 2\ Mg\ SiO_3$$

i.e., 3 Fo + 1 Q → 4 En

Therefore 3 M + 1 Q → 4 P

Similarly for felspars—

$$K\ Al\ SiO_4 + 2\ SiO_2 \rightarrow K\ Al\ Si_3\ O_8$$

i.e., 3 Kp + 2 Q → 5 Or

Therefore 3 L + 2 Q → 5 F

Thus the points P and F (Fig. 5) would represent the saturated minerals Pyroxenes and Felspars and the straight line PF, which is the saturation line, would divide the whole field into the unsaturated area PFLM and saturated area PQF.

To trace the crystallization of the charnockites in the above mentioned diagram it is necessary to start with a certain parent magma which on differentiation is capable of giving rise to the various rock types that are met with in this series.

Though there is difference of opinion regarding the nature of primary magma, there is, however, a greater agreement among petrologists regarding the universality of parent magma.

It has been found that the parent magmas for the various well-known Petrographic suites are very much allied in composition corresponding in general to a gabbro (Table VI). Their Q-L-M values when plotted in the Triangular diagram, fall within a small region, adjoining, but well below the line PF. Within this region of parent magmas falls the rock type A which has values very close to those of plateau basalt. It is interesting to note that the hornblende-norite (Type A) of the writer, of Washington (1916) and the Basicgarnetiferous norite of Groves (1935) when plotted in the Q-L-M diagram fall very close to one another.

In the diagram the dotted line encloses the field of the Calc-alkaline province. The area near about A is the area of the "mother" magma.

TABLE VI

Rock type	Q	L	M	*k*	*n*	*mg.*	*γ*	Magma type
1 Tholeiite, Ophiolithe	33·3	33·3	33·3	0·2	0·35	0·4–0·6	0·24	Gabbrodioritisch
2 Norite	33·3	33·3	33·3	0·1	0·66	0·66	0·15	c-gabbroid bis miharaitisch
3 Plateaubasalte	26·7	33·3	40·0	0·15	0·5	0·5	0·15	Normal gabbroid
4 Oceanite	20	20	60	0·2	0·5	0·5	0·1	Hornblendeperidotisch bis hornblenditisch
5 Alkalibasalte ..	16	36	48	0·25	0·35	0·55	0·25	Kaulaitisch
6 ,, ..	20	40	40	0·23	0·35	0·6	0·22	Essexitgabbroid bis essexitgabbrodioritisch
7 Tephrite bis Trachy dolerite	20	50	30	0·23	0·2	0·4	0·25	Normal theralitisch
8 Hornblende-norite (Type A of the author)	26·8	31·6	41·6	0·17	0·35	0·32	0·214	Melagabbrodioritisch
9 (Washington)	27·2	30·8	42·0	0·17	n.d.	0·36	n.d.	..
10 Basic-garnetiferous norite (Groves)	26·5	31·3	42·2	0·04	n.d.	0·58	n.d.	..

From the diagram it can be seen that there are four possible trends of differentiation as shown by the four arrows radiating from the centre of the field. They are:—

1. Norite to Anorthosite .. .. A to F
2. Norite to Pyroxenite .. .. .. A to P
3. Norite to Peridotite .. .. .. A to M
4. Norite to Granite .. .. .. towards Q

Among these four trends the charnockites of the Madras area when plotted indicate the 2nd and 4th. The second trend gives rise to types as that of Pyroxenite from Pallavaram. The fourth trend of differentiation gives rise to the more and more acid types resulting in granites.

It will be interesting at this stage to see whether the courses of crystallization followed by the charnockite as deduced from the Q-L-M diagram are to any extent reflected in the Niggli's theoretical diagram (1938, 645, Fig. 12) for the Crystallization-Differentiation of the Circum Pacific Suites.

In Fig. 6 the rock type A *viz.*, Hb.—Norite, the parent magma of the charnockites, when plotted falls in the olivine field. When cooling takes place olivine separates and the melt moves towards the peritectic line 2–4 with the result that the olivine is absorbed with the formation of pyroxene (pyroxenite) until the melt reaches 4. The above assumptions of the crystallization of olivine and its reabsorbtion gets support from the report of Holland

(1900 A, 167) who says that olivine has been observed in some slides. Washington (1916) also reports of the same in his slides.

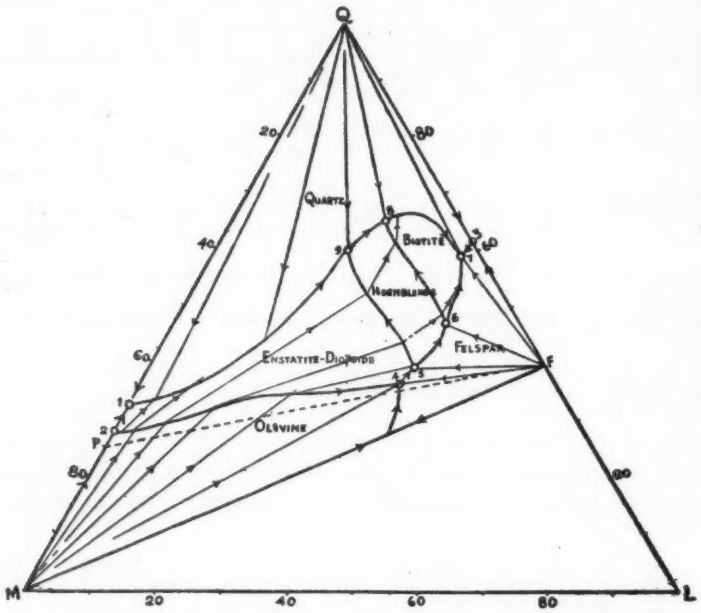

Fig. 6. Crystallization–Differentiation of the Parent Magma for the Pacific Suite (From Niggli 1938, p. 645)

When all the olivine has been absorbed the melt moves from 4 to 5 with the crystallization of En-Di and felspars, producing the rock types like B and C. The melt then moves along 5 to 6 and should have given rise to types having good amount of hornblende, but what is seen is that En-Di persists here also. This is most probably due to the charnockite magma being " dry ", hence hornblende could not crystallize out. When the melt reached 6, the mineral association should have been felspars, hornblende biotite (and quartz). But due to the " dryness " of the magma, the monoclinic pyroxene persisted, and instead of biotite an aluminous hypersthene (*vide* Part I) has crystallized giving rise to quartz-hypersthene-diorites. These rocks though not present in the writer's collection are, however, reported by previous workers such as Holland (1900), Washington (1916), Rama Rao (1945).

If the melt takes the course 6–8 then it gives rise to type D. The magma after reaching 8 takes a turn and proceeds towards 7, where there is a

simultaneous crystallization of felspars, quartz and biotite (here hypersthene) resulting in rocks like E. and F.

If, however, it follows the line 6–7 still the same rock types are evolved.

Thus the courses of crystallization followed by the charnockite magma agree even in many details to that of the theoretical diagram constructed by Niggli for the Crystallization-Differentiation of Calc-alkaline Suites.

These Circum Pacific trends of differentiation are also clearly brought out when the inter-relation of the three Basis molecules Kp-Ne-Cal is studied. The relation is usually expressed as

$$\pi = \frac{\text{Cal}}{\text{Kp} + \text{Ne} + \text{Cal}}$$

So that π gives the ratio of normative anorthite to the total normative felspars.

To bring about the relation between the above mentioned three Basis molecules, they are plotted in the above trilinear diagram (Fig. 7). The value k is measured on the side Kp-Ne with 100% k at Kp. π is measured either along the side Ne-Cal or Kp-Cal with 100% π at Cal and any particular

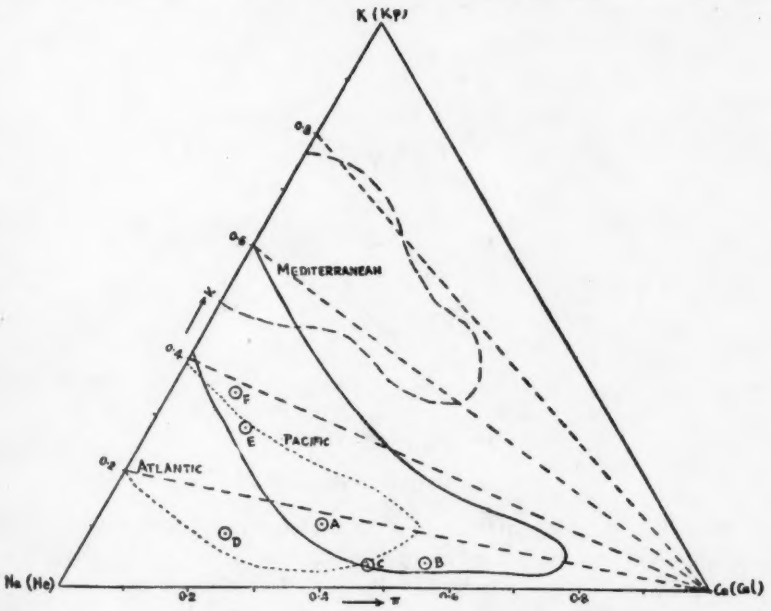

FIG. 7. π—k Diagram

value of π is got by drawing parallel lines to the side Kp-Ne. Lines joining the Cal corner from Kp-Ne side will give particular values of k.

For the sake of clarity and comparison the three fields constructed by Niggli (1938, Fig. 2*b*, 3*b* and 4*b*) for the three main petrographic suites are included here in a simplified form in the same figure.

Similar idea is got by plotting in $\gamma - mg$ diagram (Fig. 8) where

$$\gamma = \frac{Cs}{Fo + Fa + Cs}$$

so that γ gives the proportion of normative wollastonite to the total ferromagnesium minerals.

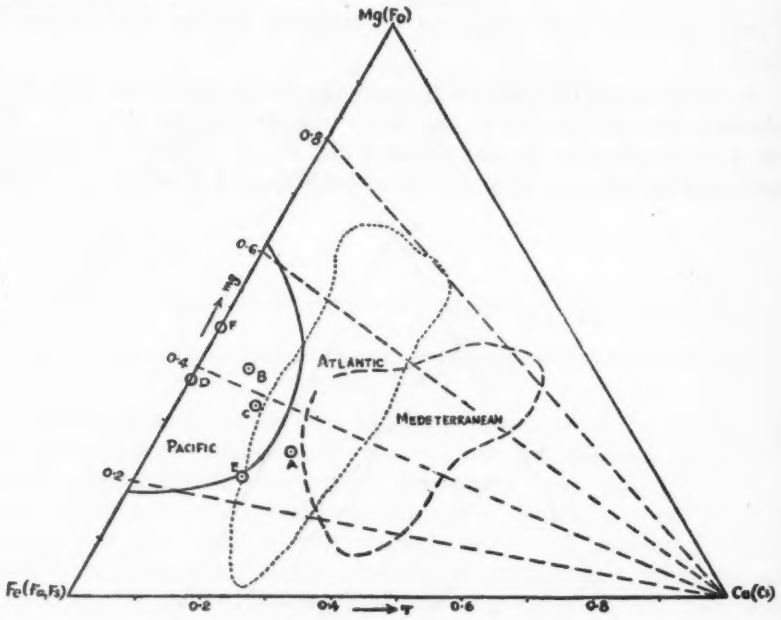

FIG. 8. γ—mg. Diagram

PETRO PROVINCIAL ASPECTS

From the foregoing study it is clear that the charnockites show a very strong affinity to the calc-alkaline or Circum Pacific Suite of rocks. It will now be worth while to see whether the typical tendencies exhibited by the differentiation diagrams can be traced in other well-known calc-alkaline Suites.

The type area of the calc-alkaline suites, *viz.*, the younger mountain chains surrounding the Pacific Ocean has been subjected to an extensive study by Burri (1926) who classified them into three main groups of differentiation tendencies within the North American Cordillera.

I. Pelee-Lassen Peak and Electric Peak.

II. Sierra Nevada (eruptives) and San Francisco Mountains.

III. Yellowstone National Park and its Sub-type Rosita.

The different interpolated values of these groups along with those of the charnockites are given in Table VII and plotted in Fig. 9.

It will be seen that Interpolated values of the charnockites agree closely with those of the above types in general and with Electric Peak in particular. On closer scrutiny it may be seen that the *fm* values of the charnockites are consistently higher than any of the types, a fact attributable to their having large amounts of hypersthene and other femic minerals.

TABLE VII

si	*al*						*fm*					
	PLP	EP	SN	YNP	NAC	CH	PLP	EP	SN	YNP	NAC	CH
120	24	26	22½	22	22½	20	41	42	43	44	42½	47
150	28½	29	27	30	27	28	36	37	36	35	35	40
200	34	31	33	35	34	32	28	32	28	27	26	35
250	38	36	38	40	38	36	22½	26	22	21	20	30
300	41	42½	41½	42	41½	40	18	18	18	17	15½	24
350	43	45½	43½	43½	44½	41	14	13	14	14	12½	20
400	45	47½	45	45	46½	43	12	11	12	11	10	17
450	46	48	46	46	48	45	10	9	10	9	7½	16

si	*c*						*alk*					
	PLP	EP	SN	YNP	NAC	CH	PLP	EP	SN	YNP	NAC	CH
120	26	25	24½	24	25	25	8	7	9½	11	10	8
150	25	23	24	20	23	21	10	11	13	15	15	11
200	22½	10½	21	17	18	18	15	17½	18	21	22	15
250	19½	17	17	13	15	15	20	21	23	26	27	19
300	16	15	12	11	14½	12	25	25	28	31	29	24
350	13	11	9	9	10½	11	30	29	33	34	33	28
400	10	8	7	8	8	8	33½	34	36	36	35	32
450	8	6	5	7	5½	6	36	37	39	38	40½	33

TABLE VII—(*Contd.*)

si	(*al-alk*)						*c*-(*al-alk*)					
120	16	19	13	11	12½	12	+10½	+ 6	+11½	+13	+12½	+13
150	18½	18	14	15	12	17	+ 6½	+ 5	+10	+ 5	+11	+ 4
200	19	14½	15	14	12	17	+ 3½	+ 5	+ 6	+ 3	+ 6	+ 1
250	18	15	15	14	11	17	+ 1½	+ 2	+ 2	− 1	+ 4	− 2
300	16	17½	13½	11	12½	16	0	− 2½	− 1½	0	+ 2	− 4
350	13	16½	10½	9½	11	13	0	− 5½	− 1½	−½	−½	− 2
400	12½	13½	9	9	11½	11	− 3½	− 5½	− 2	− 1	− 3½	− 3
450	10	11	7	8	7½	12	− 2	− 5	− 2	− 1	− 2	− 6

si	*alk*/*al-alk*						*qz* or *si*-(100+4 *alk*)					
	PLP	EP	SN	YNP	NAC	CH	PLP	EP	SN	YNP	NAC	CH
120	0·30	0·37	0·69	1·00	0·80	0·67	− 12	− 8	− 18	− 22	− 20	− 12
150	0·54	0·61	0·93	1·00	1·24	0·65	+ 10	+ 6	− 2	− 10	− 10	+ 6
200	0·79	1·20	1·20	1·50	1·83	0·88	+ 40	+ 30	+ 28	+ 16	+ 12	+ 40
250	1·11	1·40	1·53	1·85	2·77	1·12	+ 70	+ 66	+ 58	+ 46	+ 42	+ 74
300	1·56	1·43	2·07	2·81	2·31	1·50	100	100	88	76	84	114
350	2·30	1·75	3·18	3·60	3·00	2·16	130	134	118	114	118	138
400	2·67	2·50	4·00	4·00	3·03	2·91	166	164	156	156	160	172
450	3·60	3·46	5·55	4·75	5·40	2·75	206	202	194	198	188	218

PLP — Pelee Lassen Peak
EP — Electric Peak
SN — Sierra Nevada
YNP — Yellow Stone National Park
NAC — North American Cordillere
CH — Charnockites

From a perusal of the table and the differentiation diagrams (Figs. 9*a* to 9*f*) it will be seen that the Electric Peak type agrees very closely with the Charnockites. An examination of the Isofalic points (Table VIII) also points out that the Madras charnockites while agreeing well with all the types do so particularly with the Electric Peak.

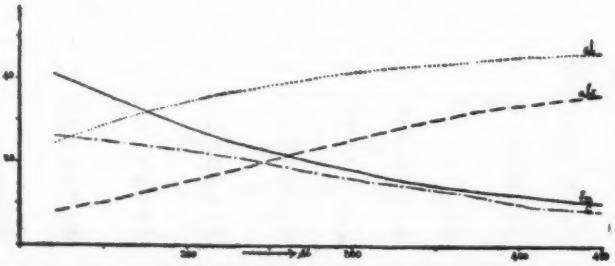

FIG. 9*a*. Differentiation Diagram of the Pelee Lassen Peak

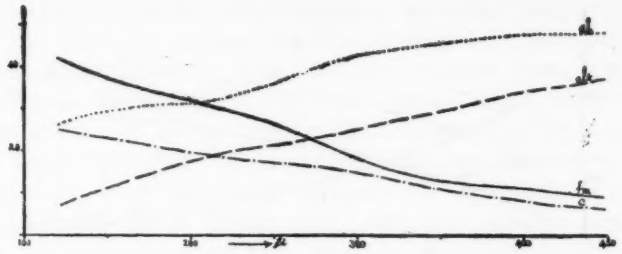

FIG. 9 *b*. Differentiation Diagram of the Electric Peak

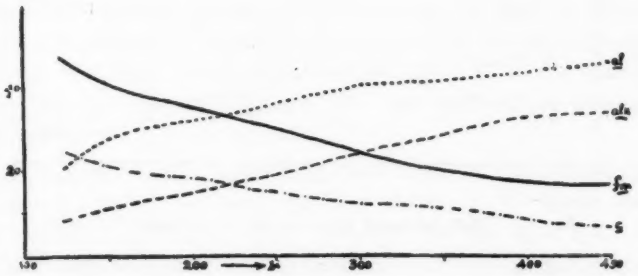

FIG. 9 *c*. Differentiation Diagram of the Sierra Nevada

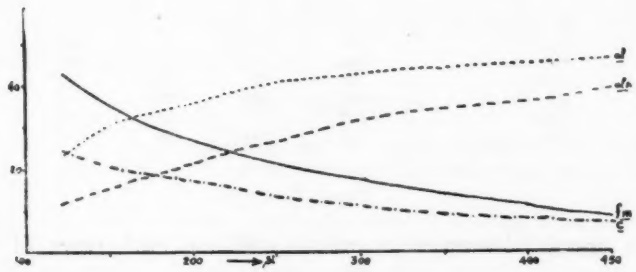

FIG. 9 *d*. Differentiation Diagram of the Fellow Stone National Park

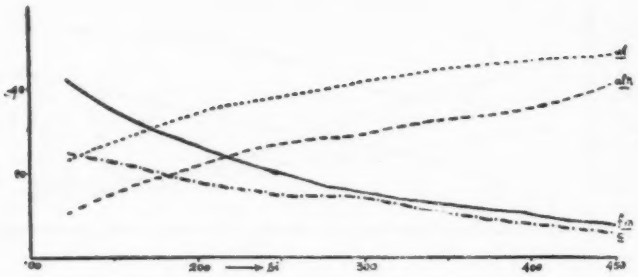

FIG. 9 *e*. Differentiation Diagram of the North American Cordillere

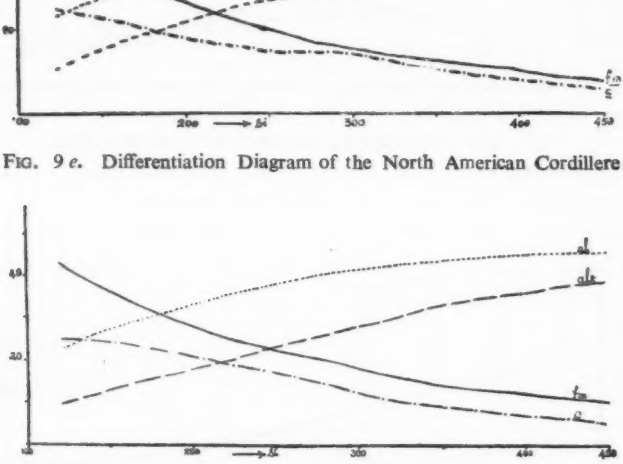

FIG. 9 *f*. Differentiation Diagram of the Charnockite Series

Thus, it is clear that the trends of differentiation exhibited by the charnockites belong to the Circum Pacific Province with close affinities in particular to the Electric Peak type.

TABLE VIII

	si	*al* = *fm*	*c*	*alk*
PLP ..	175	31·5	24	13
EP ..	206	31·5	19	18
YNP ..	167	32	19	17
SN ..	180	31	22	16
NAC ..	172	30	21	19
CH ..	216	33·5	17	16

PETROGENESIS

The chemical composition of the different rock types of this series ranging from the acid through intermediate to basic and ultra basic, occurring in close association in field after the fashion of igneous rocks, their lenticular

habit, the presence of such unstable minerals as pyroxenes and the absolute freshness of the rocks, led Holland (1900 A) to assign the charnockites an igneous origin, admitting at the same time that in some cases, they might have suffered some metamorphism at later stages. Several authors since Holland who worked on similar types in different parts of the world have given divers modes of origin to the charnockites from the nature of the local evidence. A recent Bulletin of the Mysore Geological Department (Bulletin No. 18) by Mr. B. Rama Rao, Director, Mysore Geological Department, admirably sums up these views to which reference is invited. So far as the charnockites of St. Thomas Mount, Madras, are concerned a chemical study of the rocks based on Niggli's interpretation points to an igneous origin, the diversity of the types having been brought about by magmatic differentiation.

Attention may be drawn to the fact (*vide* Part I, p. 329) that the plagioclase felspars of this series are mostly twinned after an obscure twin law *viz.*, Albite-ala or its variation, irrespective of the rock type. *Prima facie* it appears rather strange that they, in all the rock types, obey a very uncommon twin law. This becomes quite intelligible with the appreciation that all these rock types are genetically connected.

The problem of charnockites being undoubtedly very complicated, the writer does not expect, that what has been stated in this paper shall cover the whole of this complicated series. Nevertheless the facts made available here are sufficient to throw some positive light on the elucidation of its genesis, in the type area.

Acknowledgement

In conclusion, I wish to express my grateful thanks to Dr. K. P. Rode for his guidance and help throughout the course of these investigations; to Dr. Rajnath, for the facilites he gave me to carry out these investigations, and to Doctors M. S. Krishnan, C. Mahadevan and G. W. Chiplonker for the helpful suggestions and editing.

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THE REFRACTIVE DISPERSIVE POWER OF ORGANIC COMPOUNDS

Part I. The Refractive Dispersion of Dextro, Lævo and Racemic Forms of Borneol, Camphor, Camphoric Acid, Camphoric Anhydride and Camphor Carboxylic Acid

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Received July 14, 1947

In this series of investigations on the refractive dispersion of organic compounds, we describe, in this part, our experiments on enantiomeric and racemic forms of five terpene derivatives. The earlier formulæ of Gladstone and Dale[1] $\left(\frac{n-1}{d}\right)$ and of Lorenz and Lorentz[2] $\frac{n^2-1}{(n^2+1)d}$ for refractive power neglect the effect of dispersion. This effect cannot be neglected especially in the case of substances in which the wavelengths of the characteristic absorption bands controlling the dispersion are not far removed from those of the spectral region for which observations are made.

Maxwell[3] in 1869 proposed the following dispersion equation in the form of a question set at the Mathematical Tripos examination in the University of Cambridge:

$$n^2 = a^2 + \Sigma \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}.$$

This equation was also put forward by Sellmeier in 1871 and is known as the Maxwell-Sellmeier or shortly the Sellmeier equation for refractive dispersion. It is very similar to the Drude equation[4] for rotatory dispersion:

$$[\alpha] = \Sigma \frac{k_0}{\lambda^2 - \lambda_0^2}.$$

Each term of the summation in the two equations has two constants. In the Drude equation the two constants are k_0 (rotation constant) and λ_0^2 (dispersion constant). Similarly the Sellmeier equation has two constants, b_0 (refraction constant) and λ_0^2 (dispersion constant). In addition there is the constant term a^2, which when added to the summation term represents the square of the refractive index of the medium for a stationary electric field.

Both the rotatory dispersion equation of Drude and the refractive dispersion equation of Sellmeier suffer from the same defect: they do not take

into account the degradation of light energy due to absorption and thus break down when measurements are made in the region of absorption, as the influence of the neglected friction term begins to make itself felt.

The Dispersion Constant λ_0^2:

As far as theoretical and experimental evidence goes, λ_0^2 the dispersion constant which represents the square of the wavelength of the dominant absorption band, controlling the refractive dispersion and optical rotation of the medium appears to be identical in both cases. Lowry's[5] work on the rotatory dispersion of quartz in the visible region of the spectrum gives the following equation for rotatory power:

$$\alpha = \frac{11 \cdot 6064}{\lambda^2 - 0 \cdot 010527} + \frac{13 \cdot 42}{\lambda^2 - 78 \cdot 22} - \frac{4 \cdot 3685}{\lambda^2}$$

in which α represents the rotation in degrees per millimetre for a given value of λ.

Gifford's values[6] for the refractive index of quartz for the ordinary ray fit in a Sellmeier equation:

$$n^2 = 1 \cdot 35375 + \frac{1 \cdot 00317\,\lambda^2}{\lambda^2 - 0 \cdot 010627} - \frac{0 \cdot 8275\,\lambda^2}{\lambda^2 - 78 \cdot 22}$$

in which the values of λ_0's (the wavelengths of the dominant absorption bands) are those derived from Lowry's equation of rotatory dispersion of quartz above mentioned.

Pickard and Hunter[7] measured the natural rotatory dispersion, refractive dispersion and absorption spectrum of *d*-γ nonyl nitrite and found the following almost identical values of λ_0 in the three cases:

$\lambda_0 = 3680$ Å U. (rotatory dispersion measurements),

$\lambda_0 = 3730$ Å.U. (from measurements of refractive index),

$\lambda_0 = 3670 - 3720$ Å.U. (from direct photographic measurements of absorption).

It, thus, appears that the characteristic absorption bands which rotatory dispersion and refractive dispersion equations predict have a real existence and are identical.

It is with a view to place this relation on a sure experimental foundation that we have undertaken in this and subsequent papers the determination of the wavelengths of the dominant absorption band (λ_0) from measurements of refractive dispersion.

The substances employed in the present investigations are the *d*-, *l*- and *dl*- forms of borneol, camphor, camphoric acid, camphoric anhydride and camphor carboxylic acid. The rotatory dispersion of camphor carboxylic acid will be described in a separate communication and that of the other four compounds in their dextro and lævo forms has already been reported by one of us.[8] The refractive dispersion of these compounds for the *d*-, *l*- and *dl*- forms are given in Tables III to VII. The observed and calculated values of refractive index for the five wavelengths for the three stereoisomeric forms as shown reveal remarkable agreement, the differences between the observed and calculated values being within 1 part in 7000. In these Tables III to VII, the rotatory dispersion equations[8] for the compounds are also given alongside the refractive dispersion equations for the sake of comparison of their dispersion constants (λ_0^2). In Table I, the values of λ_0 as derived from rotatory dispersion and refractive dispersion measurements are given.

TABLE I

Comparative Tabular Statement of Values of (1) "*Absolute*" *rotation* (*Drude Equation*); (2) "*Absolute*" *refractive index* (*Sellmeier equation*); (3) *the wavelength of the dominant absorption band from Drude and Sellmeier equations in Å.U.*

Compound	$[\alpha]^*_{abs.}=k_0$ (Drude eqn.)	$n^*_{abs.}=\sqrt{a^2+b_0(1+\lambda_0^2)}$ (Sellmeier eqn.)	λ_0 (from Drude eqn.)	λ_0 (from Sellmeier eqn.)
Borneol ..	11·8	1·3591	1921	1962
Camphor ..	..	..	{2950 1924	1912
Camphoric acid ..	14·84	1·3596	2184	2231
Camphoric anhydride ..	0·3041	1·3555	..	2076
Camphor carboxylic acid	16·94	1·3605	2550	2589

* The values of $[\alpha]_{abs}$ and n_{abs} are calculated for the wave-length at which $\lambda^2-\lambda_0^2=1$ square micron.

The differences between the values of λ as deduced from rotatory dispersion equation and refractive dispersion equation range from 12 Å.U. in the case of camphors to 47 Å.U. for camphoric acids. For Borneols this difference is 41 units. The agreement between the two values of λ is therefore very close. Camphor has a complex rotatory dispersion represented by a two-term Drude equation*

$$[\alpha]=\frac{21\cdot91}{\lambda^2-0\cdot087}-\frac{11\cdot50}{\lambda^2-0\cdot037}$$

* This equation is recalculated from data given in Table III of Singh and Mahanti's paper (*Proc. Ind. Acad. Sci.*, A, 1935, **2**, 389).

which gives two absorption bands at λ 1924 Å.U. and λ 2950 Å.U. The refractive dispersion equation of Sellmeier gives only one band at λ 1912 Å.U., which corresponds to one of the characteristic absorption bands at λ 1924 Å.U. deduced from rotatory dispersion equation. The other band corresponding to λ 2950 Å.U. is not revealed by the three-constant Sellmeier equation as we have taken only one term in the summation. If a second term of the summation is also taken, it will result in a five-constant equation. The evaluation of this equation will be a tedious mathematical operation and it will be futile to attempt it as two out of the five spectral lines for which observations were taken are too close, namely Na_{5893} and H_{5876}. In fact as we have only 4 lines for the refractive index measurements, it is impossible to calculate the five-constant Sellmeier equation having two terms in the summation. It is, therefore, not possible to find out the second dominant absorption band λ 2950 Å.U. from the refractive dispersion equation with the present data. The direct determination of the absorption of camphor in alcohol gives a band whose maximum is at λ 2874 Å.U. according to Baly[9] *et al.*, and at λ 2890 Å.U. according to Hartley.[10] These are nearly identical in wavelengths with the second band at λ 2950 Å.U. deduced from the rotatory dispersion equation. In the graphs of Baly and Hartley, there is a second band whose maximum is not reached at λ 2200 Å.U. and may be considerably below this wavelength. As it is in the far ultra violet region, it has not yet been determined. It appears, however, that it may correspond to the band at λ 1912 Å.U. and λ 1924 Å.U. deduced from refractive dispersion and rotatory dispersion equations respectively.

These results furnish strong evidence in support of the Drude equation of rotatory dispersion and the Sellmeier equation of refractive dispersion. It, thus, appears that there is an intimate connection between optical rotatory power and refractive index. Livens[11] in 1913 deduced theoretically such a relationship which was subsequently tested experimentally by Peacock.[12] More recently, however, Condon[13] has put forward a theoretical expression connecting rotatory power with refractive index, namely,

$$\alpha = \frac{16\pi^3 N_1 \beta}{\lambda^2} \cdot \frac{n^2+2}{3}$$

but as it contains a parameter β which is not easily capable of evaluation except in some very simple cases, it has not so far found any general application.

In the case of the other substances investigated, the wavelengths of the characteristic absorption bands lie in the remote and not easily accessible spectral region in the ultra violet and a direct verification of the existence of

these bands deduced from the Drude and Sellmeier equations has not yet been realised.

Relation between Rotatory Power (Drude Equation) and Refractive Index (Sellmeier Equation) at corresponding conditions of wavelength

In previous communications,[14] the elimination of dispersion for the proper correlation of rotatory power with chemical constitution has been emphasised. For substances which exhibit simple dispersion and obey Drude's one-term equation, $\alpha = \frac{k_0}{\lambda^2 - \lambda_0^2}$ this may be easily done by making $\lambda = \sqrt{1 + \lambda_0^2}$ and calling this the "absolute wavelength"; k_0, the rotation constant, then becomes numerically, though not dimensionally, equal to $[\alpha]$ the rotatory power of the medium. This "absolute wavelength" is not much greater than 10,000 Å.U. in the infra-red region of the spectrum. Comparisons of optical rotatory power at this wavelength at which $\lambda^2 - \lambda_0^2 = 1$ square micron, may be regarded as those for corresponding conditions of wavelength, in which the effects of dispersion are eliminated. The values of $[\alpha]$ abs. or k_0 for the wavelength at which $\lambda^2 - \lambda_0^2 = 1$, for the four compounds showing simple dispersion are given in Table I. There is, however, no such easy process available for the complex type of dispersion as exhibited by camphor.

In the same way in studies on refractive index, the effect of dispersion may be eliminated for substances which obey Sellmeier's equation with only one term in the summation, namely, $n^2 = a^2 + \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2}$. The expression for the absolute value of refractive index, n_{abs}, for the "absolute wavelength" at which $\lambda^2 - \lambda_0^2 = 1$ square micron, is as below:

$$n_{abs} = \sqrt{a^2 + b_0 (1 + \lambda_0^2)}.$$

These "absolute" values of refractive indices are also given in Table I. On comparing $[\alpha]_{abs.}$ and $n_{abs.}$ (Table I) for the "absolute wavelength", it is evident that although there is no simple mathematical relationship between them, yet a rough parallelism in their values is discernible. In other words, the compound having higher value of $[\alpha]_{abs.}$ shows higher value of $n_{abs.}$ and *vice versa*. This indicates that there is some connection between rotatory power and refractive index.

Case of Camphoric Anhydride

The rotatory dispersion of *d*- and *l*- camphoric anhydrides was determined by Singh and Mahanti[8] and it was found that the compounds had zero

rotation for the wavelength range λ 6709 to 4358 Å.U. This apparent inactivity is not due to racemisation as the anhydrides on hydrolysis furnish the corresponding camphoric acids of the correct rotation. The anhydride ring is responsible for this phenomenal depression in rotation. Lowry,[15] however, gives $[\alpha]_D = -1°$ for *d*- camphoric anhydride in chloroform. Making use of this value of $[\alpha]_D$ and that of $\lambda_0^2 = 0{\cdot}0431$, deduced from the refractive dispersion equation of Sellmeier (Table VI), the Drude equation for camphoric anhydride for the D-line may be written thus:

$$[\alpha]_D = -1° = -\frac{k_0}{(\cdot 5893)^2 - 0{\cdot}0431}$$

whence $k_0 = 0{\cdot}3041$

and $$[\alpha]_\lambda = -\frac{0{\cdot}3041}{\lambda^2 - 0{\cdot}0431}$$

The Rotatory dispersion Table No. XIII given in the earlier paper of Singh and Mahanti[8] may, therefore, be modified and substituted by Table II given below.

TABLE II

Rotatory Dispersion of d- *Camphoric Anhydride in Chloroform*

$[\alpha]_\lambda^{28°} = -\frac{0{\cdot}3041}{\lambda^2 - 0{\cdot}0431}$ $\quad \lambda_0 = 2076$ Å. U.

Wave-length	Specific rotation
Li_{6708} ..	−0·75°
Cd_{6438} ..	0·82
Li_{6104} ..	0·93
Na_{5893} ..	1·00
Hg_{5780} ..	1·04
Hg_{5461} ..	1·19
Ag_{5209} ..	1·33
Cd_{5086} ..	1·41
Hg_{4358} ..	2·07

Physical Identity of Enantiomers

Pasteur's Law of Molecular Dissymmetry[16] holds good rigidly both as regards the vectorial and scalar properties of optically active and their opposite isomers. Numerous recent measurements on rotatory dispersion[17] have confirmed the truth of this law. A series of measurements of their scalar properties such as viscosities[18] has demonstrated that this law applies equally rigidly in their case also. The law was also shown to hold good as regards refractive index.[18] These earlier measurements were made with an Abbe refractometer. Our present measurements (Tables III to VII) are made

with a Pulfrich Refractometer for five wavelengths in the visible region of the spectrum from λ 6563 Å.U. to λ 4359 Å.U. The refractive indices are identical for the *d*- and *l*- forms within an accuracy of about 1 part in 7,000. The refractive indices of the racemic forms (1 per cent. solution in ethyl alcohol) are identical with those of their optical isomers within about 1 part in 7000. It thus appears probable that the racemates in dilute solution are completely dissociated into their components.

Experimental

The dextro, lævo and racemic forms of borneol, camphor, camphoric acid and camphoric anhydride were prepared and purified according to the methods described by one of us.[8] Camphor carboxylic acids were prepared according to the method of Bredt.[19,20]

The refractive indices were determined with a Pulfrich Refractometer, jacketed with water from a thermostat maintained at 35° C. and may be regarded accurate to 0·0002 unit. The concentration of the solution in absolute alcohol was one per cent., namely, one gram in 100 c.c. of solution, in all cases except camphoric anhydrides for which 0·625 per cent. solutions were made due to their low solubility. The experimental results are given in Tables III to VII.

Table III

Refractive Dispersion of l-, d- *and* dl-*Borneols* : $C_8H_{14}\begin{cases}CH_2\\ |\\ CHOH\end{cases}$

$$n^2 = 1{\cdot}6890 + \frac{0{\cdot}1524\lambda^2}{\lambda^2 - 0{\cdot}0385}\,; \qquad \lambda_0{}^2 = 0{\cdot}0385$$

$$\left\{ [\alpha]^{*}_{\lambda} = \frac{11{\cdot}80}{\lambda^2 - 0{\cdot}03692} \quad ; \quad \lambda_0{}^2 = 0{\cdot}03692 \right\}$$

λ	n calculated (*c*)	n lævo (*l*)	$n_{l\text{-}c}$	n dextro (*d*)	$n_{d\text{-}c}$	n racemic (*r*)	$n_{r\text{-}c}$
H_{6563} ..	1·3625	1·3626	+·0001	1·3627	+·0002	1·3624	−·0001
Na_{5893} ..	1·3640	1·3642	+·0002	1·3641	+·0001	1·3639	−·0001
H_{5876} ..	1·3640	1·3641	+·0001	1·3641	+·0001	1·3640	±·0000
Hg_{5461} ..	1·3653	1·3652	−·0001	1·3653	±·0000	1·3655	+·0002
Hg_{4359} ..	1·3712	1·3710	−·0002	1·3710	−·0002	1·3712	±·0000

* This equation is calculated from rotatory dispersion data given in Table XV of Singh and Mahanti's paper (*Proc. Ind. Acad. Sci.*, A, 1935, **2**, 394).

TABLE IV

Refractive Dispersion of l-, d- *and* dl- *Camphors*: $C_8H_{14}\begin{cases}CH_2\\ |\\ C=O\end{cases}$

$$n^2 = 1{\cdot}6657 + \frac{0{\cdot}1742\lambda^2}{\lambda^2 - 0{\cdot}0366}; \qquad \lambda_0{}^2 = 0{\cdot}0366$$

$$\left\{ [\alpha]^*_\lambda = \frac{21{\cdot}91}{\lambda^2 - 0{\cdot}087} - \frac{11{\cdot}50}{\lambda^2 - 0{\cdot}037} \qquad \begin{matrix}\lambda_0{}^2 = 0{\cdot}037\\ \lambda_1{}^2 = 0{\cdot}087\end{matrix} \right\}$$

λ	n calculated (*c*)	n lævo (*l*)	$n_{l\text{-}c}$	n dextro (*d*)	$n_{d\text{-}c}$	n racemic (*r*)	$n_{r\text{-}c}$
H_{6563} ..	1·3624	1·3622	−·0002	1·3623	−·0001	1·3624	±·0000
Na_{5893} ..	1·3640	1·3639	−·0001	1·3639	−·0001	1·3640	±·0000
H_{5876} ..	1·3640	1·3641	+·0001	1·3641	+·0001	1·3641	+·0001
Hg_{5461} ..	1·3654	1·3653	−·0001	1·3652	−·0002	1·3653	−·0001
Hg_{4359} ..	1·3717	1·3716	−·0001	1·3717	±·0000	1·3715	−·0002

* This rotatory dispersion equation has been re-calculated from data given in Table III of Singh and Mahanti's paper (*Proc. Ind. Acad. Sci.*, A, 1935, **2**, 389).

TABLE V

Refractive Dispersion of l-, d-, *and* dl- *Camphoric Acids*: $C_8H_{14}\begin{cases}COOH\\ |\\ COOH\end{cases}$

$$n^2 = 1{\cdot}7277 + \frac{0{\cdot}1153\lambda^2}{\lambda^2 - 0{\cdot}0489}; \qquad \lambda_0{}^2 = 0{\cdot}0489$$

$$\left\{ [\alpha]^*_\lambda = \frac{14{\cdot}84}{\lambda^2 - 0{\cdot}0477} \qquad \lambda_0{}^2 = 0{\cdot}0477 \right\}$$

λ	n calculated (*c*)	n lævo (*l*)	$n_{l\text{-}c}$	n dextro (*d*)	$n_{d\text{-}c}$	n racemic (*r*)	$n_{r\text{-}c}$
H_{6563} ..	1·3630	1·3629	−·0001	1·3630	±·0000	1·3631	+·0002
Na_{5893} ..	1·3645	1·3647	+·0002	1·3645	±·0000	1·3647	+·0002
H_{5876} ..	1·3645	1·3646	+·0001	1·3646	+·1001	1·3645	±·0000
Hg_{5461} ..	1·3659	1·3658	−·0001	1·3657	−·0002	1·3660	+·0001
Hg_{4359} ..	1·3722	1·3722	±·0000	1·3721	−·0001	1·3720	·0002

* This rotatory dispersion equation is taken from Table V of Singh and Mahanti's paper (*Proc. Ind. Acad. Sci.*, A, 1935, **2**, 390).

TABLE VI

Refractive Dispersion of l-, d- *and* dl- *Camphoric Anhydrides*:

$$C_8H_{14}\begin{cases}CO\\CO\end{cases}O$$

$$n^2 = 1{\cdot}6900 + \frac{0{\cdot}1412\lambda^2}{\lambda^2 - 0{\cdot}0431}; \qquad \lambda_0{}^2 = 0{\cdot}0431$$

$$\left\{[\alpha]^*_\lambda = \frac{0{\cdot}3041}{\lambda^2 - 0{\cdot}0431}\right\}$$

λ	n calculated (*c*)	n lœvo (*l*)	$n_{l\text{-}c}$	n dextro (*d*)	$n_{d\text{-}c}$	n racemic (*r*)	$n_{r\text{-}c}$
H_{6563} ..	1·3591	1·3590	−·0001	1·3590	−·0001	1·3592	+·0001
Na_{5893} ..	1·3607	1·3608	+·0001	1·3609	+·0002	1·3608	+·0001
H_{5876} ..	1·3607	1·3607	±·0000	1·3608	+·0001	1·3608	+·0001
Hg_{5461} ..	1·3621	1·3621	±·0000	1·3621	±·0000	1·3622	+·0001
Hg_{4359} ..	1·3685	1·3685	±·0000	1·3685	±·0000	1·3684	−·0001

* This rotatory dispersion equation is calculated by using $\lambda_0{}^2$ deduced from the refractive dispersion equation given in this Table.

TABLE VII

Refractive Dispersion of l-, d-, *and* dl- *Camphor Carboxylic Acids*:

$$C_8H_{14}\begin{cases}CH_2\\|\\CH\cdot COOH\end{cases}$$

$$n^2 = 1{\cdot}7765 + \frac{0{\cdot}0699\lambda^2}{\lambda^2 - 0{\cdot}0670}; \qquad \lambda_0{}^2 = 0{\cdot}0670$$

$$\left\{[\alpha]^*_\lambda = \frac{16{\cdot}94}{\lambda^2 - 0{\cdot}0650}\right\} \qquad \lambda_0{}^2 = 0{\cdot}0650$$

λ	n calculated (*c*)	n lævo (*l*)	$n_{l\text{-}c}$	n dextro (*d*)	$n_{d\text{-}c}$	n racemic (*r*)	$n_{r\text{-}c}$
H_{6563} ..	1·3635	1·3635	±·0000	1·3635	±·0000	1·3636	+·0001
Na_{5893} ..	1·3650	1·3649	−·0001	1·3649	−·0001	1·3649	−·0001
H_{5876} ..	1·3650	1·3650	±·0000	1·3651	+·0001	1·3651	+·0001
Hg_{5461} ..	1·3663	1·3661	−·0002	1·3663	±·0000	1·3664	+·0001
Hg_{4359} ..	1·3727	1·3727	±·0000	1·3727	±·0000	1·3727	±·0000

* Unpublished results.[20]

SUMMARY

1. The refractive dispersion of dextro, lævo and racemic forms of borneol, camphor, camphoric acid, camphoric anhydride and camphor

carboxylic acid has been determined in alcohol at 35° C. for five wavelengths. The values of the refractive indices are identical for the three forms and fit in a Sellmeier equation.

2. The equality of the refractive indices of the dextro and lævo forms supports Pasteur's Law of Molecular Dissymmetry.

3. The values of λ_0, the wavelength of the characteristic absorption band, calculated from the Sellmeier refractive dispersion equations are in remarkable agreement with those deduced from the Drude rotatory dispersion equations.

4. A rotatory dispersion equation for camphoric anhydride, which cannot be determined from its rotatory power data, has been deduced by employing λ_0 calculated from the Sellmeier refractive dispersion equation.

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STUDIES ON THE NATURE OF THE RACEMIC MODIFICATION OF OPTICALLY ACTIVE COMPOUNDS

Part VII. Solubility and Melting Point Studies of Active and Inactive Camphorcarboxylic Acids

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Received May 16, 1947

THE Solubility-Composition isotherms of camphoric acids[1,2] and camphor-β-sulphonic acids,[3] have been studied in earlier parts of this series with a view to determine the nature of their racemic modifications. Both the acids give rise to curves consisting of three parts, corresponding to (*a*) *d*-acid in presence of *dl*-acid, (*b*) *dl*-acid in presence of *d*- and and *l*-acids and (*c*) *l*-acid in presence of *dl*-acid. Following the methods of Roozeboom,[4] and Bruni,[5] it was concluded that the racemic forms of both the acids were true *dl*-compounds. On the other hand, the curves would have consisted of only two parts in the case of the *dl*-mixture (one portion corresponding to the *d*-acid in presence of *l*-acid, and the other corresponding to *l*-acid in presence of *d*-acid) there being no separate phase due to the *dl*-form which is merely an equimolecular mixture of the *d*- and *l*-forms.

The freezing-point (melting-point) method, also due to Roozeboom, had been applied to these and other compounds.[6] Theoretically, the freezing point-composition curves should in general be quite similar to the solubility-composition isotherms: a racemic mixture giving rise to two sections with a minimum of temperature (eutectic point), a racemic compound to three sections with two eutecit and the mixed crystal type giving rise to one single continuous curve. The results obtained from the solubility method were in complete agreement with those derived from the freezing point method.

In the present paper, we have applied both these methods to the study of the inactive form of camphor carboxylic acid. The two methods lead to the same conclusion, namely, that the racemic acid is a *dl*-compound.

EXPERIMENTAL

The *d*-, *l*- and *dl*-camphorcarboxylic acids were prepared by a method due to Bredt.[7] Dry carbon dioxide gas was passed into an ethereal solution of camphor containing sodium beads at room temperature (25° C.). The initial vigorous reaction subsided after a time, when it was found that

the reaction mixture had become quite thick. In order that all the sodium may react, it was found advisable to warm the reaction mixture, when it became less viscous and reaction proceeded smoothly. After nearly all the sodium beads had been used up, powdered ice was added and the aqueous extract kept for 24 hours. On warming to about 50° C., most of the borneol formed during the reaction was precipitated out. The camphor carboxylic acid was obtained by acidifying the filtrate. The crude acid was recrystallised several times from warm aqueous alcohol (10%). Melting point: *d*- and *l*- acids 128–129°; *dl*-acid 135–136° C. $[\alpha]_{5461}^{35°} = \pm 84{\cdot}0°$ in 0·5% aqueous solution.

The measurements of solubilities were made in an apparatus described in Part III of this series.[1] For the determination of the percentage composition at the isothermal invariant points, the specific rotation of the active form, at a concentration equal to the total acids present, was extrapolated (see discussion) and this value used in calculating the amount of the active form present. The results are given in Tables II and III.

TABLE I. *Rotation of camphorcarboxylic acid in aqueous solution at* 30° *C.*

Conc. in gms. per 100 gms. of water	Rotation in 2-dcm. tube for Hg_{5461}	$[\alpha]_{5461}^{30°}$
0·16	0·24	75·0°
0·30	0·48	80·0
0·375	0·61	81·33
0·50	0·84	84·0
0·60	1 12	93·33
0·72*	1·52	105·5
0·81	1·82†	112·35

* Saturated solution. † Extrapolated value.

TABLE II. *Solubility of mixtures of d- and dl-camphor carboxylic acids in water at* 30° *C.*

Total acids (gms./100 gms. of water)	Amount of *d*-acid	Amount of *dl*-acid	Percentage Composition	
			dl-acid	*dl*-acid
·723	·723	..	100·0	0·0
·737	·687	·050	93·2	6·8
·771	·671	·100	87·0	13·0
·815	·654	·161	80·3	19·7
·729	·571	·158	78·3	21·7
·572	·402	·170	70·0	30·0
·506	·321	·185	63·5	36·5
·429	·161	·268	37·8	62·2
·411	·080	·331	19·5	80·5
·411	..	·411	0·0	100·0

TABLE III. *Solubility of mixtures of l- and dl-camphorcarboxylic acids in water at 30° C.*

Total acids (gms./100 gms. of water)	Amount of *l*-acid	Amount of *dl*-acid	Percentage Composition	
			l-acid	*dl*-acid
·717	·717	..	100·0	0·0
·751	·701	·050	93·3	6·7
·781	·681	·100	87·2	12·8
·817	·652	·165	79·8	20·2
·670	·503	·167	74·6	25·4
·538	·361	·177	67·1	32·9
·467	·241	·226	51·6	48·4
·413	·120	·293	29·1	70·9
·411	..	·411	0·0	100·0

The freezing point method had to be modified as the substance decomposes into camphor and carbon dioxide on prolonged heating, and quick determinations had therefore to be made. In view of this, the melting points, instead of the freezing points, were determined. Mixtures were prepared by directly weighing out known amounts of the components and mixing them well in an agate mortar. Six determinations were made with each mixture, and the average value taken to minimise any errors arising in the mixing of the components and the determination of the melting points. The results are given in Tables IV and V.

TABLE IV. *Melting points of mixtures of d- and dl-camphorcarboxylic acids*

Percentage Composition*		Melting point
d-acid	*dl*-acid	
100	..	129·2°
90	10	123·4
80	20	122·2
70	30	121·0
60	40	120·8
50	50	121·4
40	60	124·6
30	70	130·0
20	80	132·2
10	90	135·0
..	100	136·0

* By weight

TABLE V. *Melting points of mixtures of l- and* dl-*camphorcarboxylic acids*

Percentage Composition*		Melting point
l-acid	*dl*-acid	
100	..	129·0°
90	10	125·0
80	20	121·8
70	30	121·0
60	40	120·7
50	50	121·5
40	60	125·8
30	70	129·6
20	80	132·5
10	90	134·4
..	100	136·0

DISCUSSION

The experimental results of solubility determinations given in Tables II and III are plotted in Fig. 2 showing total solubility in grams per 100 grams of water against the percentage composition. The determination of the isothermal invariant points presented certain difficulties as the specific rotation was found to vary with concentration. The specific rotation of camphor carboxylic acid in water at 30° was determined at several concentrations up to the point of saturation (Table I). There is a noticeable increase in the value of $[\alpha]_{5461}^{30°}$ with concentration. While working with mixtures of active and inactive acids containing known amounts of the active substance, it was noticed that the measured rotation corresponded to the amount taken, if the specific rotation at the concentration of the total acids present, was used for calculating the amount of the optically active acid. These results can be explained if it be assumed that the specific rotation of the undissociated acid is greater than that of the dissociated acid. Numerous examples of a similar variation in specific rotation with concentration are known as in the case of mandelic acids[8] and several camphorates.[9]‡ In subsequent investigations,[10] on the rotation of camphor carboxylic acid in different solvents, it was noticed that the specific rotation varied within wide limits depending upon the acidic or basic nature of the solvent. This lends further support to the view that the effect may be

* By weight

‡ Solutions of camphoric acid in alcohol and acetone are also mentioned by Landolt as behaving in a similar way. The aqueous solutions of camphoric acid (studied in earlier parts did not, however, show any measurable change in specific rotation in the range investigated) although the alcoholic solutions did show some variation.[9]

ascribed to dissociation. The specific rotation corresponding to the total acids present at the isothermal invariant point was, therefore, extrapolated (Fig. 1), and this value used in the calculation of the amount of active acid present.

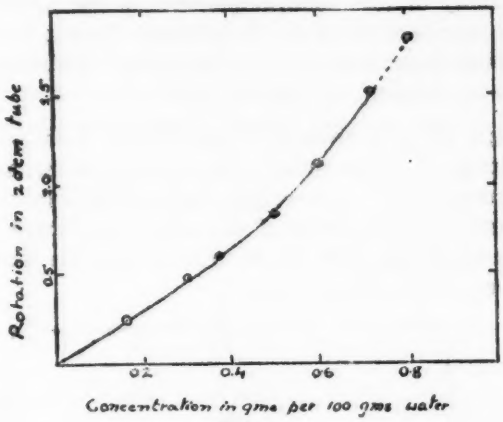


FIG. 1

The solubility-composition isotherm for mixtures of active and inactive camphor carboxylic acids in water at 30°, given in Fig. 2, consists of three

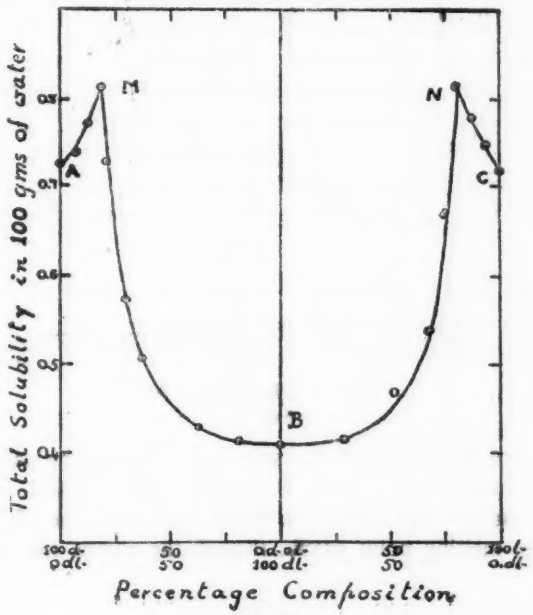


FIG. 2

sections, AM, MBN and NC. AM corresponds to the solubility of the *d*-acid in presence of the *dl*-acid. The first half MB of MBN corresponds to the solubility of the *dl*-acid in presence of *d*-acid while the second half BN corresponds to its solubility in presence of *l*-acid. The portion CN shows the solubility of the *l*-acid in presence of the inactive form. The existence of the two isothermal invariant points M and N and the nature of the graph obtained indicate that inactive camphor carboxylic acid exists as a compound in solution in water at 30° C.

The melting point data given in Tables IV and V are plotted in Fig. 3, percentage composition of the mixtures being the abscissæ and the melting points the ordinates. Here also we get a well defined maximum with two prominent minima. The presence of the central maximum in the melting point curve is a clear indication of the existence of the racemic acid as a *dl*-compound even at its melting point.

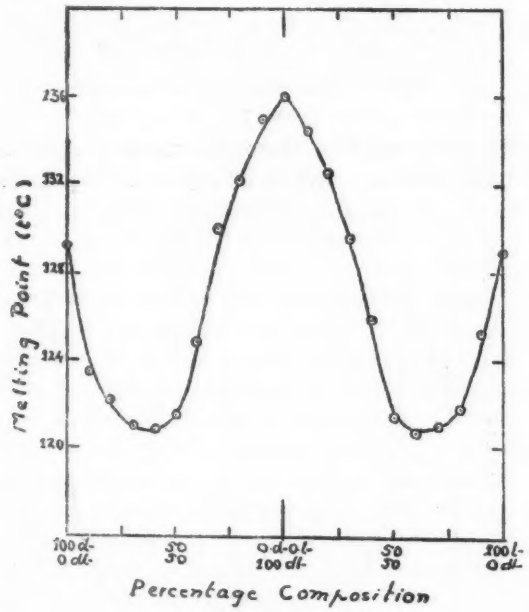
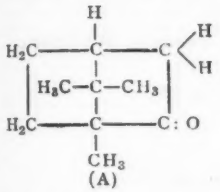


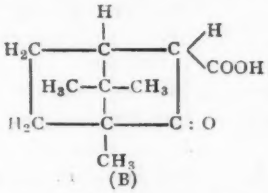
FIG. 3

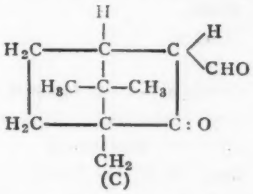
The general similarity of the solubility-composition isotherm and the melting point-composition curve is evident. The central portion in both cases is well marked indicating the stable nature of the *dl*-compound. In the case of the melting point graph, though the curves rise and fall steeply,

the eutectic points are not well defined. If we consider the *d-dl*-section of the curve (or the *l-dl*-portion) we have practically one curve only, joining the melting point of the racemic form to that of the active form. Such curves, though with less pronounced minima, are usually obtained in the formation of solid solutions. The rapid fall in the melting point of the pure *d-* and *dl-* forms in the presence of small amounts of the *dl-* or *d-* form respectively, gives indication of their existence as well defined compounds. The continuous nature of the curve near the minima, however, seems to point to the formation of mixed crystals between the active and inactive forms.

The dextro and lævo forms of camphor are well known[11] to give a series of solid solutions with nearly the same melting point throughout. Camphor carboxylic acid (B) resembles camphor (A) very closely and differs from it


(A)


(B)


(C)

only in the substitution of a $-COOH$ group for an $-H$ atom. The formation of solid solutions between the active and inactive forms of camphor carboxylic acid, though to a lesser degree, is therefore quite possible. It is of interest to note in this connection that oxymethylenecamphors (C)—in the aldehydic form—which bear a close resemblance to the camphors and the camphor carboxylic acids, were also found[12] to give curves closely akin to those obtained in the present case.

It is proposed to undertake a further analysis of the melting point curve in a subsequent paper with a view to determine the degree of dissociation of the racemic acid at its melting point.

We wish to thank the University of Allahabad, where this work was carried out, for the award of the Empress Victoria Readership in Chemistry to one of us (B.K.K.N.) and for the grant of research facilities.

Summary

(1) The solubility-composition isotherm of mixtures of active and inactive camphor carboxylic acid in water at 30° C. has been determined.

(2) The isotherm consists of three curves with two isothermal invariant points indicating the inactive acid to be a *dl*-compound.

(3) The melting point-composition curves of mixtures of active and inactive camphorcarboxylic acids have also been determined.

(4) The curve shows two well pronounced minima (eutecti) showing that the inactive acid is a *dl*-compound, in conformity with the solubility results.

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